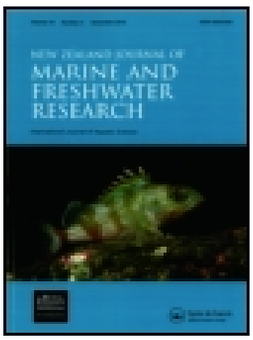

New Zealand Journal of Marine and Freshwater Research

ISSN: 0028-8330 (Print) 1175-8805 (Online) Journal homepage: http://www.tandfonline.com/loi/tnzm20

Natural dispersion of mercury from Puhipuhi, northland, New Zealand

F. E. Hoggins & R. R. Brooks

To cite this article: F. E. Hoggins & R. R. Brooks (1973) Natural dispersion of mercury from Puhipuhi, northland, New Zealand, New Zealand Journal of Marine and Freshwater Research, 7:1-2, 125-132, DOI: 10.1080/00288330.1973.9515459

To link to this article: http://dx.doi.org/10.1080/00288330.1973.9515459

NATURAL DISPERSION OF MERCURY FROM PUHIPUHI, NORTHLAND, NEW ZEALAND

F. E. HOGGINS and R. R. BROOKS

Department of Chemistry, Biochemistry, and Biophysics, Massey University, Palmerston North, New Zealand

(Received for publication 2 August 1972)

ABSTRACT

The mercury content of sediments and water in the Wairua (Wairoa) River, Northland, and of molluscs from the estuary of the river was determined to establish the extent of natural dispersion of mercury from deposits at the source of the river at Puhipuhi. The mercury content per gram wet weight of cockles, *Chione stutchburyi,* (0.032 ppm); rock oysters, *Crassostrea glomerata,* (0.081 ppm); pipi *Paphies australe,* (0.019 ppm); and green-lipped mussels, *Perna canaliculus,* (0.017 ppm) was compared with that of specimens of the same species from other areas where presumably only background concentrations exist. Mercury could be detected in sediments at least 35 km from the deposits, but in water only up to about 8 km. Normal background levels were established for the soft parts and individual organs of the four species of mollusc investigated; of the molluscs found in the estuary of the Wairua River, only *C. glomerata* had anomalous amounts of mercury, but whether this indicates abnormally high mercury levels in the environment is unknown, because many other factors still need to be evaluated. Mercury levels of all molluscs were well below the generally accepted safety level of 0.5 ppm for fish for human consumption.

INTRODUCTION

As a result of a greater awareness of the need to preserve the environment and of the development of highly-sensitive methods for analysing mercury in recent years there has been increasing interest in the effects of man-made mercury pollution on the biosphere; there have been particularly numerous studies on mercury in fish (Grimstone 1972). The concern stemmed originally from the death of 50 persons in Minamata Bay, Japan (Kurland *et al.* 1960) after their eating fish contaminated with methyl mercury from a plastics factory. At present, safety limits for foodstuffs have been set at 1.0 ppm in Japan and Sweden, and 0.5 ppm in U.S.A. and Australasia: the concentration is on a wet-weight basis for fish.

Mercury differs from other heavy metals as a pollutant because natural concentrations have always been high in fish; samples of fish bone up to 1000 years old contained similar amounts of mercury to present-day fish (Grimstone 1972). Because of this high natural level, the difference between background levels in pelagic fishes (0.01–0.10 ppm) and the recommended safety level of 0.5 ppm is quite small.

The natural dispersion of mercury deserves more study to determine its magnitude to establish standards from which man-made pollution may

be gauged. For example, mercury levels in waters near regions of geothermal activity can be extremely high; levels of up to 0.003 ppm (30 times background) have been reported (White 1967).

Mercury is also a useful indicator in the search for sulphide minerals and for the element itself. Because it is very volatile, mercury can often be detected at considerable distances from its origin, and can then be traced back to the original deposit; the development of extremely sensitive methods for the determination of mercury improves its value. Mercury may be determined now in rocks and soils (Saukov 1946, Koksoy & Bradshaw 1969), waters (White 1967), and even in the air (McCarthy *et al.* 1969). Studies of mercury in the New Zealand environment have been carried out for several years (Weissberg 1971).

The present work is an investigation into the natural dispersion of mercury from the Puhipuhi deposits in Northland along the course of the Wairua (Wairoa) River. Analyses were carried out on waters, stream sediments, and also on molluscs from the estuary. The molluscs were chosen because of the extraordinary capacity of bivalves to concentrate trace elements from their environment (Brooks & Rumsby 1965). Shellfish of the same species were obtained from other, presumably background areas, to act as controls. It was hoped that the work would both establish "normal" levels of mercury in some species of molluscs and also establish how far from the source mercury deposits might be detected by geochemical methods.

STUDY AREA

The Puhipuhi mercury deposits are situated near Whakapara, some 35 km north of Whangarei, at the source of the Waiariki River, the main tributary of the Wairua (Wairoa) River which enters the sea at Dargaville (Fig. 1). The deposits are a cinnabar-impregnated sinter which, though at present sub-economic, has been worked at various periods in the past. During the Second World War, the deposits were exploited by open-cast mining, and about 14 tonnes of mercury were produced (Williams 1965).

The cinnabar occurs either as polished pellets in gravels or more frequently as impregnations in discontinuous sinter masses which overlay a basement of greywacke, argillite, and quartzite. The deposits are capped with a basaltic flow. Present reserves are computed at 500 tonnes of mercury spread over several areas (Williams 1965).

METHODS

SAMPLE COLLECTION

Molluscs were collected in January 1972 from the estuary of the Wairua River and from other areas presumably not subject to above-normal levels of mercury: Maunganui Bluff on the west coast, and Pataua Bay and Whangarei harbour on the east.

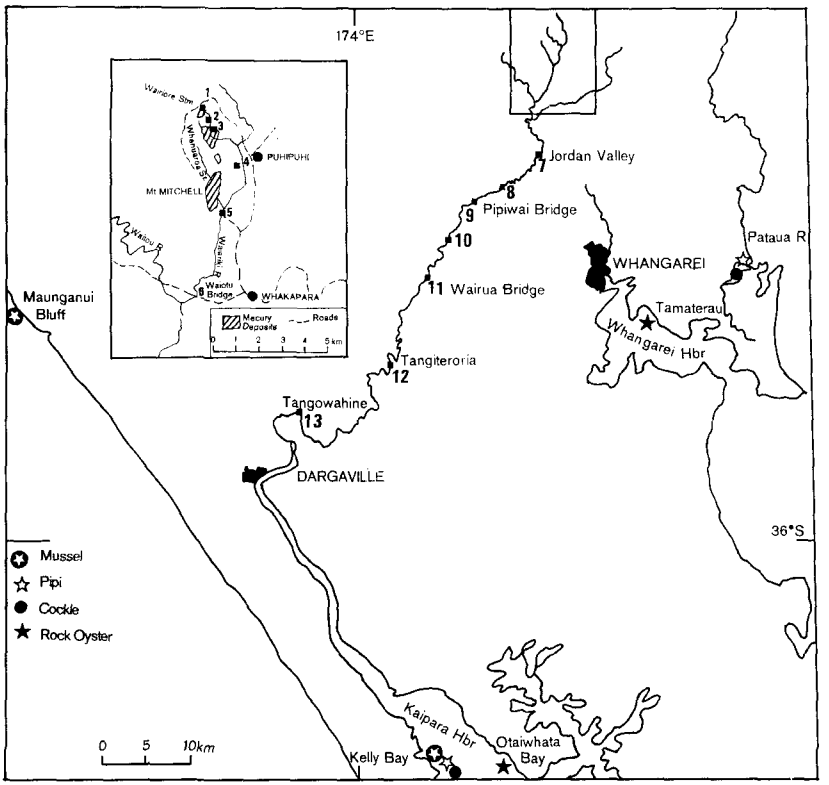

FIG. 1—Map of part of Northland, New Zealand, showing Wairua River area and (*inset*) the Puhipuhi mercury deposits. Sampling locations for stream sediments and waters (1–13) and collection sites for molluscs are also shown (mussel = *Perna canaliculus*; pipi = *Paphies australe*; cockle = *Chione stutchburyi*; rock oyster = *Crassostrea glomerata*).

Except for remote ocean beaches, most coastal and estuarine environments cannot be said to be certainly free from pollution. Only the Maunganui Bluff sample comes from such a "clean" environment; the others were from enclosed waters where pollution is always a possibility. However, Pataua River was assumed to be pollution-free because a careful study of this virtually uninhabited area showed no obvious sources of contamination. Kaipara Harbour likewise appeared to have no obvious sources of man-made pollution. Pollution of Whangarei Harbour is more likely, but a quick survey of local industry failed to establish any likely source of mercury which could have affected the rock oyster samples from Tamaterau.

Stream water samples were collected at various points along the Wairua River beginning at the Puhipuhi mercury deposits and ending about 100 km downstream, at Tangowahine near Dargaville. Sediment samples were taken at the same points as the water samples.

TABLE 1—Mercury concentrations (ppm per gram wet weight) in molluscs sampled from Wairua River estuary, and in control samples (lower of each pair). (– = not distinguished from muscle)

SPECIES	SAMPLING LOCATION	*n*	SOFT PARTS		*n*	INDIVIDUAL ORGANS					
			Mean	Range		Foot	Gills	Mantle	Muscle	Shell	Viscera
Cockle, *Chione stutchburyi* (Gray)	Kellys Bay, Dargaville	6	0.032	0.013–0.065	5	–	0.060	0.038	0.037	0.005	0.021
	Mouth of Pataua River	11	0.031	0.017–0.049	5	–	0.074	0.085	0.054	0.016	0.045
Rock oyster, *Crassostrea glomerata* (Gould)	Otaiwhata Bay, Dargaville	12	0.081	0.043–0.142	6	–	0.165	0.116	0.080	0.011	0.131
	Tamaterau, Whangarei Hbr	10	0.059	0.044–0.087	3	–	0.128	0.137	0.075	0.018	0.072
Pipi, *Paphies australe* (Gmelin)	Kellys Bay, Dargaville	10	0.019	0.009–0.036	3	0.009	0.013	0.013	0.009	0.012	0.012
	Mouth of Pataua River	10	0.023	0.014–0.034	7	0.009	0.020	0.013	0.014	0.012	0.012
Mussel, *Perna canaliculus* (Gmelin)	Kellys Bay, Dargaville	11	0.017	0.009–0.035	6	0.021	0.019	0.012	0.011	0.010	0.019
	Maunganui Bluff	10	0.017	0.011–0.022	5	0.015	0.032	0.028	0.017	0.005	0.023

ANALYTICAL PROCEDURES

Sediments were analysed by a modification of the method of Vaughn (1967). Samples of 0.2 g were sieved (0.18 mm mesh) and placed in nickel boats positioned inside a quartz tube. The sediments were then heated in a radio frequency field and the volatile gases were carried through the system in a stream of nitrogen. The mercury vapour was adsorbed on a gold plug and the other gases were vented from the system. The gold plug was then heated in the radio frequency field and the mercury was passed into an absorption chamber which had quartz windows. The mercury was determined by flameless atomic absorption using the resonance line at 254 nm and a Techtron AA3 atomic absorption spectrophotometer. The source was an Osram mercury discharge lamp operated at 2 ma current. The limit of detection of the method was 0.02 ppm for a 0.2 g sample.

Water was analysed by the method of Hinkle & Learned (1969). Approximately 100 ml of water was acidified with hydrochloric acid (to give a final concentration of 1 mol/litre H^+ ions) and a 4 cm × 4 cm piece of 0.42 mm mesh silver gauze was placed in the vessel and shaken for at least 1 hour. The gauze was washed, air-dried, and placed in the radio frequency furnace. Analysis was carried out as for the stream sediments. The limit of detection of the method was 0.0001 ppm.

Shellfish were analysed by a modification of the method of Hatch & Ott (1968). Samples (1 g wet weight) of shellfish were digested for 1 hour at 130–140°C in Kjehldahl flasks with a mixture of 5 ml concentrated sulphuric acid and 2 ml of 1:1 nitric acid. The mixtures were then cooled and diluted with 30 ml water and 4 ml of 3% hydroxylamine hydrochloride (to reduce excess nitric acid because addition of stannous chloride to residual nitric acid can result in evolution of oxides of nitrogen which cause interference problems). This was followed by 2 ml of 10% stannous chloride solution. The mixtures were stirred vigorously in Erlenmeyer flasks for 90 s and the mercury was then expelled in a stream of nitrogen and fed as before into the absorption chamber. The limit of detection was 0.005 ppm for a 1 g sample.

RESULTS AND DISCUSSION

MERCURY LEVELS IN MOLLUSCS

Mercury levels in whole animals (excluding shells) are shown in Table 1. The table also gives data for individual organs. Except for *Crassostrea glomerata*, there were no significant differences in mercury levels between molluscs collected from the mouth of the Wairua River and those obtained elsewhere. A t test on the samples of *C. glomerata* showed that the means of the two populations were significantly different at the 95% level of probability ($t = 1.96$ for 20 degrees of freedom). Although this difference in mercury levels could be due to natural mercury contamination from Puhipuhi, there is not as yet sufficient evidence to prove this conclusively, particularly as the same trend is not evident for the other species.

The results clearly show that the mercury levels in all shellfish are well below the safety limits for human consumption (0.5 ppm); the highest value recorded was 0.142 ppm in one specimen of *Crassostrea glomerata*.

When the mercury levels in individual molluscs are examined (Table 1), there are no great differences among individual organs. The visceral mass, shown by Brooks & Rumsby (1965) to be a favoured site for trace element accumulation by many species of molluscs, does not appear to have significantly greater concentrations than other organs. The concentrations of mercury are greatest in the gills and mantle though these levels are seldom more than twice as high as in other organs. The lack of selectivity of mercury uptake by different organs of all molluscs studied seems to imply that this element is not metabolised, but rather complexes with any available macromolecules via the co-ordinate link (Schubert 1954), or alternatively that it is accumulated by ion exchange on to mucus sheets, as shown for the oyster by Korringa (1952).

MERCURY LEVELS IN WATER AND SEDIMENTS

Figure 2 shows mercury levels (ppm) in water and sediments for the whole length of the Wairua River. Mercury levels decrease rapidly to background (less than 0.0001 ppm) in a little over 8 km from the source. Pecora (1970) also reported this low residence time of mercury in natural waters; he stated that mercury in solution is rapidly scavenged by sediments and particularly by organic matter in them. Thus the mercury content of stream waters will not be a very useful exploration tool in New Zealand, particularly when other variables such as flow can also cause problems (Wodzicki 1959).

Although the concentration of mercury in the water was at or near the normal background level (<0.0001 ppm) when the river reached Dargaville, a very small excess over background could have resulted in inordinately high levels in rock oysters, because of the very great capacity of certain bivalves to concentrate trace elements from their environment (Brooks & Rumsby 1965).

Sediments are a much more suitable material for detecting mercury (and presumably also sulphide mineralization, since anomalous amounts of this element (greater than 0.2 ppm) were detectable at distances up to 35 km from the deposits. Sediment samples can also be analysed more easily, contain higher levels of mercury, and give more consistent results than water samples.

We hope that this paper will stimulate further work on the use of natural mercury dispersion in prospecting, and on the effects of this element upon the marine biosphere, and also that the information will usefully augment the rapidly-growing pool of "normal" levels of mercury in molluscs.

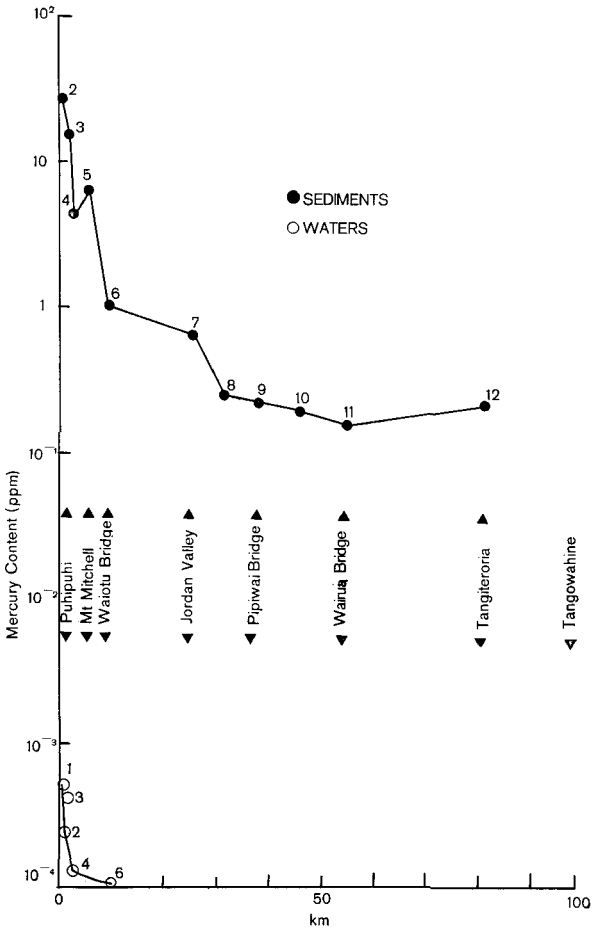

FIG. 2—Mercury concentrations (ppm) in waters and sediments of the Wairua River, 1971, shown as a function of distance from the mercury deposits. Sample location numbers are also shown; only water sample taken at Tangowahine.

CONCLUSIONS

1. Tentative pollution-free background levels per gram wet weight for molluscs are: cockle, *Chione stutchburyi*, 0.03 ppm; rock oyster, *Crassostrea glomerata*, 0.06 ppm; pipi, *Paphies australe*, 0.02 ppm; and green-lipped mussel, *Perna canaliculus*, 0.02 ppm.
2. With the possible exception of the rock oyster, none of the shellfish taken from the estuary of the Wairua River contained anomalous amounts of mercury. Further work will be needed before it can be

established with certainty that elevated amounts of mercury in rock oysters are due to the Puhipuhi deposits and not to other environmental factors.

3. The mercury content of river water is a poor indicator of the mercury mineralization as it is not effective beyond 8 km from the deposits.
4. The mercury content of river sediments appears to be a reliable and sensitive indicator and is effective up to 35 km from the deposits.

ACKNOWLEDGMENT

We are indebted to Dr B. G. Weissberg of Chemistry Division, DSIR, for extensive advice and assistance with analytical problems.

LITERATURE CITED

BROOKS, R. R. & RUMSBY, M. G. 1965: The biogeochemistry of trace element uptake by some New Zealand bivalves. *Limnology and Oceanography 10*: 521–7.

GRIMSTONE, G. 1972: Mercury in British fish. *Chemistry in Britain 8*: 244–7.

HATCH, W. R. & OTT, W. L. 1968: Determination of sub-microgram quantities of mercury by atomic-absorption spectrophotometry. *Analytical Chemistry 40*: 2085–7.

HINKLE, M. E. & LEARNED, R. E. 1969: Determination of mercury in natural waters by collection on silver screens. *U.S. Geological Survey Professional Paper 650-D*: 251–4.

KOKSOY, M. & BRADSHAW, P. M. D. 1969: Secondary dispersion of mercury from cinnabar and stibnite deposits, West Turkey. *Colorado School of Mines Quarterly 64*: 333–56.

KORRINGA, P. 1952: Recent advances in oyster biology. *Quarterly Reviews of Biology 27*: 266–308.

KURLAND, L. T., FARO, S. N. & SIEDLER, H. S. 1960: Minamata disease. *World Neurologist 1*: 320–5.

MCCARTHY, J. H. Jr., VAUGHN, W. W., LEARNED, R. E. & MEUSCHKE, J. L. 1969: Mercury in soil gas and air—a potential tool in mineral exploration. *U.S. Geological Survey Circular 609*: 16 pp.

PECORA, W. T. 1970: Mercury in the environment. *U.S. Geological Survey Professional Paper. 713*: 1–5.

SAUKOV, A. A. 1946: Geochemistry of Mercury (in Russian). *Trudy Institut geologicheskoy Nauka 78*: 1-129.

SCHUBERT, J. 1954: Interaction of metals with small molecules in relation to metal protein complexes. Pp. 11–63 *in* F. R. D. Gurd (ed.) "Chemical Specificity in Biological Interactions", Academic Press, New York. 234 pp.

VAUGHN, W. W. 1967: A simple mercury vapor detector for geochemical prospecting. *U.S. Geological Survey Circular 540*: 1–8

WEISSBERG, B. G. 1971: Determination of mercury in soils by flameless atomic-absorption spectrophotometry. *Economic Geology 66*: 1042–7.

WHITE, D. E. 1967: Mercury and base metal deposits with associated thermal and mineral waters. Pp. 575–631 *in* H. L. Barnes (ed.) "Geochemistry of Hydrothermal Ore Deposits", Holt-Rinehart-Wilson, New York. 670 pp.

WILLIAMS, G. J. 1965: "The Economic Geology of New Zealand". Australasian Institute of Mining and Metallurgy, Melbourne. 384 pp.

WODZICKI, A. 1959: Geochemical prospecting for uranium in the Lower Buller Gorge, New Zealand. *N.Z. Journal of Geology and Geophysics 2*: 602–12.