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Alkylmercury Levels in Marine Sediments in Cockburn Sound, Western Australia

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Cockburn Sound, Western Australia, as a result of development in the last thirty years, now has a number of large chemical process industries located on the eastern shore. The Cockburn Sound Study (CHEGWIDDEN 1979), set up to investigate the effects of growing industrialisation on the Sound, established that small amounts of mercury were being discharged in the gypsum - containing effluent from a fertiliser plant. It was further established that significant levels of this element were accumulating in the sediments in the immediate vicinity of the outfall.

A "gypsum mound" had in fact formed in the immediate vicinity of the outfall. This was later dredged and dispersed. It was theorised that when the mercury in the "mound" was shifted from the previous highly anaerobic environment to another more oxygenated one, this could lead to the formation of alkylmercury compounds. It was not possible to locate the dispersed material from the "mound".

However a new discharge system which achieves better dispersion has been installed in order to prevent development of a further "mound". It was thought that conditions in the new system might parallel those pertaining during dispersion of the original mound, and thus favour formation of alkylmercury. Hence sampling of seafloor sediment was carried out in a grid pattern over the present dispersal area.

The analysis of sediments for alkylmercury has been described by a number of authors (FLOYD and SOMMERS 1975; KUMAGAI and SAEKI 1977; MITANI 1976; NAGASE et al. 1980; VAN FAASSEN 1975; WESTOO 1968). Because of previous work on alkylmercury in fish samples using steam distillation, (COLLETT et al. 1980) a similar approach was favoured in this investigation. This transforms the alkylmercury to inorganic mercury using potassium persulphate. NAGASE et al. (1980) collected the distillate in dilute hydrochloric acid, and displaced the mercury from the alkyl group with copper ion Distillation was commenced at an acid strength of 4N so that even with dilution by steam the optimum acidity range of 1-4N given by MITANI (1976) would be maintained.

FLOYD and SOMMERS (1975) refer to the volatilisation of

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monomethylmercury which occurs during the addition of acid to calcareous sediments. A closed distillation system shown in Figure 1, derived from that of FLOYD and SOMMERS, was thus developed. This apparatus allows considerable space to deal with the frothing which occurs when calcareous sediments are acidified.

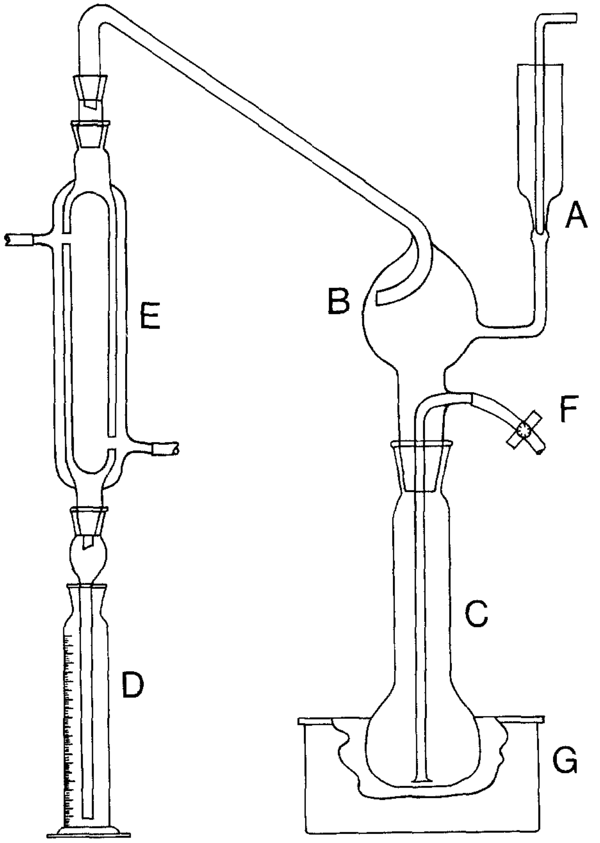

Figure 1.
A and B. Quickfit D62/50 50 mL dropping funnel with Quickfit D62/0 funnel plug fitted to modified Quickfit SH7/23 steam distillation head, sloping delivery, with downward extension to steam inlet, and with delivery tube modified to resemble Quickfit recovery bend, vertical Quickfit SH2/22. C. Kjeldahl flask, (100 mL nominal capacity), fitted with B24 ground glass joint. D. 100 mL graduated cylinder. E. Double walled condenser. F. Steam inlet with adjustable tubing pinch clip. Steam is from a generator, Buchi Glasapparate Fabrik, Flawil, Switzerland, type G.D. 1500. G. 100 mL size 60W mantle, Electrothermal (U.K.) Cat.No. M102. G is elevated and D is placed on screwjack for ease of use.

It was found that the addition of sodium chloride as suggested by NAGASE et al. (1980), following on the work of MITANI (1976), and by KUMAGAI and SAEKI (1977) did not give a recovery better than that obtained without the use of sodium chloride.

As the acidity is an important factor in distillation, it was necessary to add sufficient acid to neutralise carbonate and react with any metal sulphide present. The acid equivalence of those sediments analysed for alkylmercury ranged from 29.3-71.5 per cent as calcium carbonate on a dry weight basis.

MATERIALS AND METHODS

Sampling Samples were taken from the seafloor in a predetermined grid pattern on 8.5.80. See Figure 2.

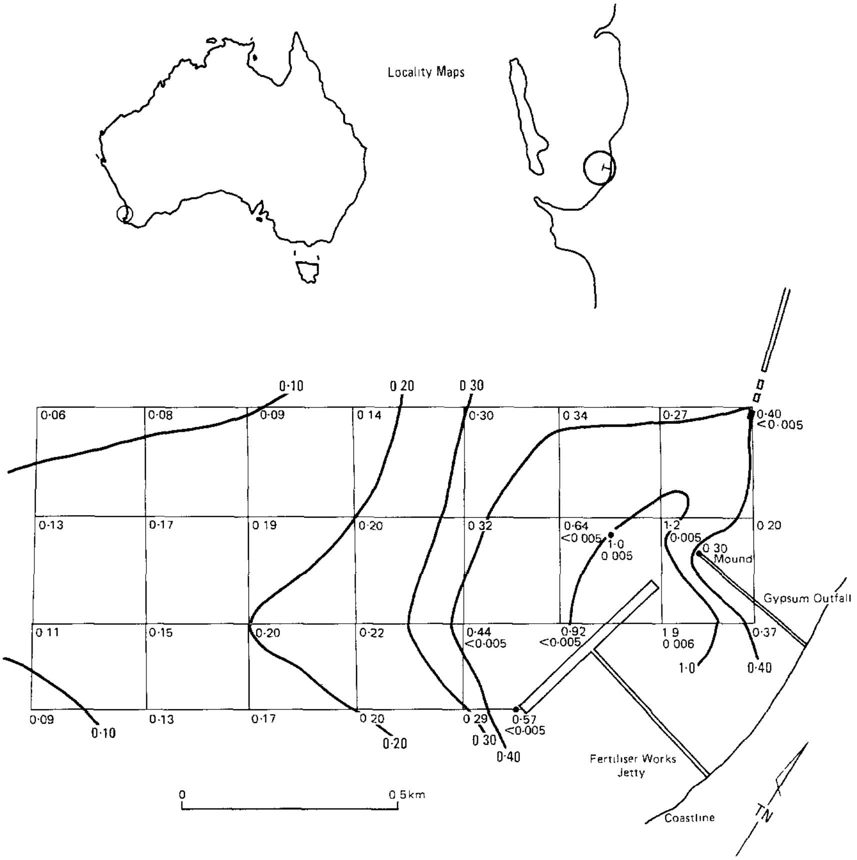

Figure 2.
Total mercury concentration isopleths in sediments near fertiliser works outfall, Cockburn Sound, Western Australia. Top figure at each point is total mercury concentration, lower figure is alkyl mercury concentration. (All figures are mg/kg Hg dry weight basis).

Water depths ranged from 2-18 m. 3 cm i.d. polycarbonate tubes with bevelled leading edges were used for sampling. At each sampling point, five of these were inserted in the sediment to a depth of approximately 10 cm, within a 1 m dia area, stoppered at each end and brought to the surface. Water was carefully removed and the core moved (by gravity or gentle blowing) until the section corresponding to the top 2 cm of seabed could be cut off. The 2 cm sections from the five cores were placed in one jar and cooled with dry ice then later stored in a freezer.

Cores to be used as control samples were taken from the non-industrialised Warnbro Sound, south of Cockburn Sound, in a similar manner.

In addition, 8 cm dia cores were taken at three of the sampling points, in addition to the principal cores taken. The larger cores were used to test for mercury in the interstitial water, that is water recovered from the core upon centrifugation. The purpose of the tests was to establish whether, in view of the somewhat variable amounts of water unavoidably included in the core sections sampled, the water made a significant contribution to the mercury content of the sediment when the sample was freeze-dried. No mercury was detected in the interstitial water.

A sample from each point was analysed firstly for total mercury. If the result exceeded 0.4 mg/kg (on a dry-weight basis), further samples from that point were analysed for alkylmercury.

Experimental

(a) Total Mercury. This is determined by a modification of the method of DEITZ et al. (1973), using approximately 2.5 g of freeze-dried sample 5 mL water, and 25 mL of digest mixture (0.25 per cent ammonium metavanadate in 2+1 sulphuric acid/nitric acid), with the 100 mL Kjeldahl flasks heated in airbath to ensure good temperature control, which is critical. After digestion, the cooled digest is diluted to 70 mL and filtered (Whatman No. 541). The flask and residue are washed with hot 5 per cent nitric acid (4 x 8 mL) and the combined filtrate and washings made up to 130 mL. Cold vapour atomic absorption spectrophotometry (HATCH and OTT 1968) is used to determine the mercury concentration.

(b) Alkylmercury.

Reagents

Absorbing solution. Slurry 2.5 g A.R. ammonium metavanadate in 220 mL concentrated sulphuric acid sp. gr. 1.84. Add the slurry carefully to 700 mL distilled water and when cool make up to 1 litre. Two per cent by weight of potassium persulphate is added to an aliquot of the solution just prior to use.

Antifoam B. Dow-Corning.

Bromothymol blue indicator solution. Dissolve 0.1 g in 1.6 mL of 0.1M sodium hydroxide and make up to 100 mL with water.

Diluting solution. Slurry 0.48 g A.R. ammonium metavanadate in 20 mL concentrated sulphuric acid, cautiously add to distilled water. Use a further 65 mL concentrated sulphuric acid to wash the slurry residue into the water and make the solution up to 1 litre with distilled water.

Hydrochloric acid/copper (II) sulphate solution. Add 50 g A.R. copper (II) sulphate to 200 mL A.R. hydrochloric acid sp. gr. 1.18. Warm gently to dissolve.

Hydrochloric acid, A.R. concentrated. sp. gr. 1.18.

Potassium persulphate solution. Dissolve 2 g A.R. potassium persulphate in 100 mL distilled water. Make up fresh as required.

Stannous chloride solution, 10 per cent m/V in 1.5M sulphuric acid. Heat on a hot plate to simmering with granulated A.R. tin. Remove sulphide impurities by bubbling nitrogen through the solution until free from the odour of hydrogen sulphide. Some residual tin should remain in the solution.

Sodium hydroxide solution A.R., 2M.

Sulphuric acid, A.R. concentrated. sp.gr. 1.84.

Standards

Methyl mercury chloride standard solution. Add 0.1304 g A.R. methyl mercury chloride to 20 mL redistilled dimethylformamide, shake to dissolve, and make up to 25 mL with dimethylformamide. Store in a deep freeze.

Methyl mercury chloride intermediate solution. Add 3 mL methyl mercury chloride standard solution to water and make up to 500 mL with water.

Methyl mercury chloride working solution. Add 3 mL methyl mercury chloride intermediate solution to water and make up to 500 mL with water. This solution contains 0.150 µg/mL (as Hg) of methyl mercury chloride. Make up fresh daily. This solution should be assayed for methyl mercury content using the method, as a check on degradation.

Procedure

5 mL of 2N sodium hydroxide solution is added to the marine sediment (100-200 g) and then the sediment is freeze-dried for 12 hours with a plate temperature of 10°C in an acid washed flat glass dish, to a final pressure of 7 Pa. The mass before and after can be measured if a moisture figure is required. It is then milled for 30 seconds in a rotary ring mill (Type T-100, N.V. Tema, 's Gravenhage, The Netherlands), placed in a jar and mixed.

Determination of Amount of Acid Needed to Neutralise Sediment. Weigh 2-3 g of sediment accurately into a 150 mL Erlenmeyer flask. Add 20.0 mL of standardised 2M hydrochloric acid solution, cover with a watchglass and leave to stand with occasional stirring for 15 minutes. Wash the underside of the watchglass with distilled water, adding this to the flask.

Add 1 mL of bromothymol blue solution and titrate the residual acid with standardised 1M sodium hydroxide solution.

Distillation. 2.5 g - 3 g of the sediment is then weighed accurately into a 100 mL Kjeldahl flask fitted with a B-24 ground glass socket such that the total length of the flask is 245 mm. The amount of hydrochloric acid/copper (II) sulphate solution (x mL) needed to neutralise the mass of sample taken is calculated. Two drops of Antifoam B are added. 3 mL of hydrochloric acid/copper (II) sulphate solution is placed in the top funnel of the apparatus followed by x mL of concentrated hydrochloric acid and 5.0 mL water. 25 mL of absorbing solution is added to the 100 mL graduated cylinder and the cylinder is raised on a jack so that the condenser outlet is immersed almost to the bottom of the solution.

With the apparatus assembled and the water flowing at a rate of ca. 3.5 L/min through the double-walled condenser, the mixture in the top funnel is added quickly to the Kjeldahl flask and the unit immediately resealed.

The isomantle under the distillation flask is heated for 1.5 min at full voltage and steam is then admitted slowly to the flask. When major foaming has ceased, the rate of steam flow is increased such that the distillation rate is 13 mL/min. After 45 mL has been collected the graduated cylinder is lowered and the isomantle and steam flow are turned off. The delivery tube of the condenser is washed with ca 3 mL of water, collecting the washings in the cylinder.

The absorbing solution is transferred quantitatively to a 150 mL Erlenmeyer flask, washing with 2 x 5 mL of potassium persulphate solution. After 5.5 mL concentrated sulphuric acid is added to the flask, the solution is heated on a boiling water bath for 50-60 minutes.

When the solution has cooled, it is transferred quantitatively to a 100 mL measuring cylinder, made up to 100 mL and mixed.

Determination. The mercury content of the solution is then measured by the cold vapour technique using a mercury analyser, adding diluting solution to dilute the sample if the mercury content is high.

RESULTS AND DISCUSSION

The results of the analyses are shown in Figure 2.

after initial analysis of thirty two sampling points for total mercury a clear pattern of mercury distribution emerged for thirteen points. Samples from the other nineteen points whose relationship was less obvious were further analysed until consistent values were obtained. Then, as previously mentioned, selected points were analysed for alkylmercury.

The quantities of alkylmercury represent the mean of three or more determinations. The recovery of methylmercury chloride from spiked sediment samples, adding the spike before freeze-drying, was 88 per cent. The total mercury content of the spiked samples before and after freeze-drying was the same, so that the loss occurred in the distillation step, not the freeze-drying. Elemental sulphur distilled over in some of the samples. Tests using spiked samples with added sulphur (10 mg) showed this had no effect on recoveries.

The results indicate that significant biomethylation has not occurred in the area described.

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