GERBAM — Deuxième Colloque International de Bactériologie marine — CNRS, Brest, 1-5 octobre 1984
IFREMER, Actes de Colloques, 3, 1986, pp. 35-42

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CHEMICAL AND MICROBIOLOGICAL ASPECTS OF ACOUSTICALLY TURBID SEDIMENTS

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ABSTRACT - The methane concentrations within both Holyhead harbour and Western Irish sea sediments were consistent with the hypothesis that methane was the major component responsible for the acoustic turbidity, which is in agreement with Anderson and Hampton (1980 a) and Vilks and Rashid (1977). Microcosm experiments indicate that, for Holyhead harbour methanogenesis may be the major contributor to the methane pool held within the sediment. Furthermore sulphate-reducing bacteria, although natural competitors for the most probable subtrates of methanogenesis, may be limited in their activity by sulphate concentrations at the depths where methane is being produced.

Key words: gassy sediment, methanogenesis, acoustic turbidity.

RÉSUMÉ - Les concentrations de méthane dans les sédiments du port de Holyhead et de la partie occidentale de la mer d'Irlande sont en compatibles avec l'hypothèse selon laquelle le méthane est le principal composé responsable de la turbidité acoustique, ce qui est en accord avec les résultats de Anderson et Hampton (1980a) et Wilks et Rashid (1977). Des expériences en microcosme indiquent que dans le cas du port de Holyhead, sinon pour la mer d'Irlande, la méthanogénèse peut être la source principale du méthane des sédiments. De plus, les bactéries sulfato-réductrices, bien que compétiteurs naturels pour la plupart des substrats de la méthanogénèse, peuvent être limitées par les concentrations des sulfates existant aux profondeurs où le méthane est produit.

Mots clés: sédiment, méthanogénèse, turbidité acoustique.

INTRODUCTION

Acoustically turbid sediments contain gas bubbles, minimum diameter between 1 μm and 10 μm, held within unconsolidated fine sediment, which cause scattering of sound waves generated by subbottom profiling equipment (Anderson and Hampton, 1980 a) These gas bubbles reduce the shear strength gradients in fine sediments. In North sea sediments gas plumes have been linked to the production of pockmarks (cone shaped depressions possibly caused by gas/fluid migration) which represent a threat to the stability of structures placed on the seabed (Hovland and Gudmestad, 1984).

Our interest centres round the origin and nature of the gases within unconsolidated fine sediments. Hovland and Gudmestad (1984) consider that two major sources of gas and fluid exist capable of causing pockmarks, either biogenic (shallow) gas formed in shallow surface layers, or thermogenic (deep seated) gas and fluid from hydrocarbon reserves. Gas formed in organically rich sediments is usually a consequence of the anaerobic breakdown of organic matter, as oxygen is present in only the top few centimetres, and may include carbon dioxide, methane, nitrogen, ammonia or hydrogen sulphide. The considerations governing bubble formation and gaseous composition were discussed by Anderson and Hampton (1980 a, b). It was demonstrated by Anderson and Hampton (1980 a),

working on freshwater lakes in Texas, and by Vilks and Rashid (1977), working on the sediments of St Margarests Bay in Canada, that the major component of the gas bubbles causing acoustic scattering in the sediments under study was methane.

The complete anaerobic breakdown of organic matter involves a number of metabolically separate microorganisms interacting to yield carbon dioxide and methane as end products. Intermediate products of anaerobic metabolism are fatty acids and hydrogen, which then act as substrates for the sulphate-reducing and methane-producing bacteria, the terminal organisms in the anaerobic microbial food chain. Considerable interest in the nature of the interaction between sulphate-reducing and methane producing bacteria has been shown over recent years (Cappenberg and Prins, 1974 ; Oremland and Taylor, 1978 ; Winfrey and Ward, 1983) specifically in the way that sulphate concentrations influence both microbial groups (Oremland and Polcin, 1982 ; Lovley, Dwyer and Klug, 1982 ; Lovley and Klug, 1983 ; King, Klug and Lovley, 1983 ; Kristjansson, Schonheit and Thauer, 1982 ; Schonheit, Kristjansson and Thauer, 1982).

Analysis of the methane concentrations within acoustically turbid sediments from the Western Irish Sea and Holyhead Harbour are reported below. Microcosm experiments demonstrating the potential for biogenic methane production causing the acoustic turbidity are also described.

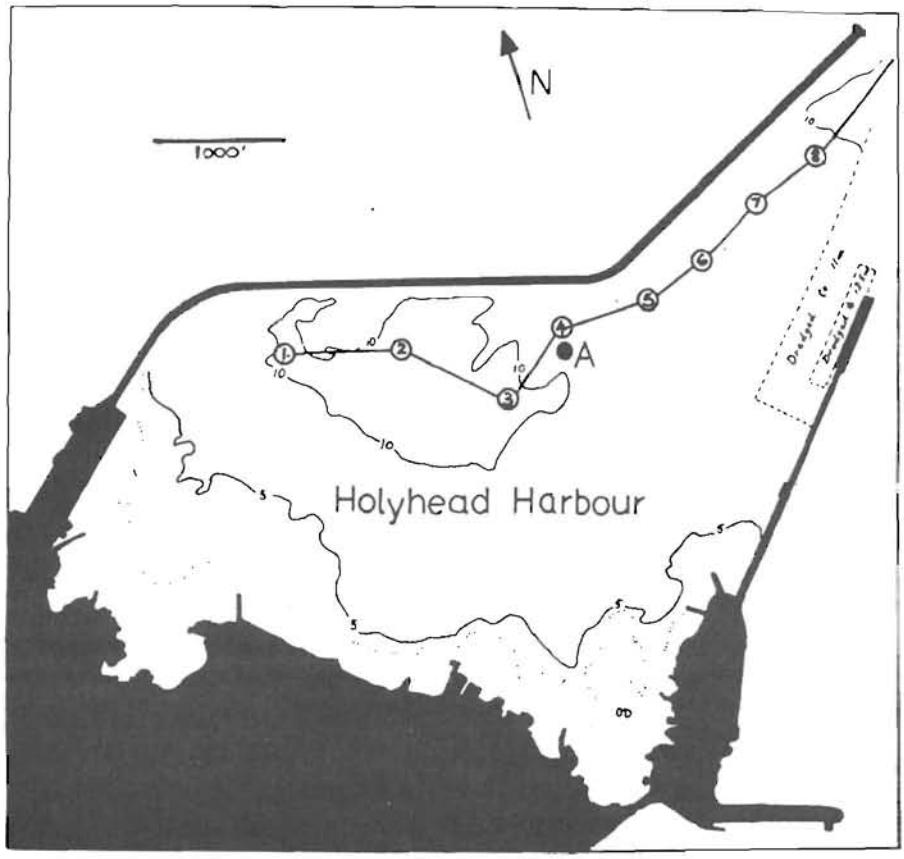

Figure 1 : Map of Holyhead harbour and sampling stations.

MATERIALS AND METHODS

Study sites and field methodology

Holyhead Harbour. The inner harbour contains extensive areas of acoustically turbid anoxic sediment at a depth of approx. 10 m. During March 1982 core samples were taken and acoustic traces were recorded for a series of sample stations (Fig. 1). Additional mud cores were obtained for the microcosm experiments.

Western Irish Sea. A deep water site (approx 100 m) west of the Isle of Man has deposits of up to 30 m of Holocene mud which is acoustically turbid. Three separate sampling cruises were made during the periods May 1982, April 1984 and July 1984 (Fig. 2). Core samples were taken and sub-bottom acoustic traces were recorded at each sampling station.

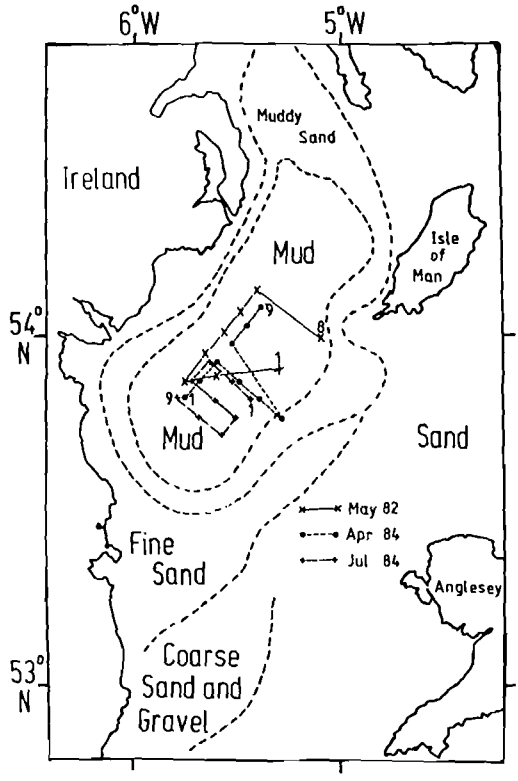

Figure 2 : Map of the Western Irish sea and sampling stations.

Coring. A 7 cm diameter hydroplastic gravity corer was deployed from the RV Prince Madog in order to collect cores between 60 cm and 200 cm long.

Acoustic sub-bottom profiling. An ORE Inc. Model 140 10 KW Transceiver linked to hull mounted ORE Inc. Transducers (Ocean Research Equipment Inc., Massachussetts) was operated at 5 KW output for all sub-bottom profiling. Output of the trace was via a Gifft series 4000 facsimile recorder (Hydro Products (UK) Ltd., Aberdeen).

Core sub-sampling. A series of sampling ports were drilled at 20 cm intervals into the plastic core tubes, which were then fitted with air tight seals. Samples were removed from the core using disposable plastic syringes, transferred to gas tight tubes, and were stored in the freezer prior to analysis for methane gas.

Pore water extraction from Holyhead harbour sediments. Pore water was extracted at ambient temperature under nitrogen using six Reeburg squeezers operated off a single manifold. 10 ml aliquots were retained for dissolved methane analysis (Mc Auliffe, 1971). About 20 ml of the pore water was retained frozen for the analysis of dissolved organic carbon, volatile organic carbon and sulphate ion.

Analytical techniques.

Methane. Concentrations of methane within Holyhead harbour and Western Irish sea sediments were determined by gas chromatography. A Perkin Elmer F 11 (Perkin Elmer Ltd., Beaconsfield) containing a 3 m glass lined metal column, packed with 80-100 mesh Poropak N (Phase Separations Ltd., Queensferry) operated at 70° C, with OFN (BOC Ltd., London) carrier gas flowing at 30 ml min^{-1}, was used for some analyses. Alternatively a Dani SPA 3 800 HR GC (Kontron instruments Ltd., St. Albans) containing a 1.5 m pyrex column packed with Poropak QS (Phase Separations Ltd., Queensferry), operated at 120°C, injector temperature 150°C, detector temperature 150°C, with OFN (BOC Ltd., London) carrier gas flowing at 30 ml min^{-1} was used for analysis. The FID detectors were calibrated with standard gas mixtures (Phase Separations Ltd., Queensferry). Headspace gases were sampled through septa with either 100 μl or 1 ml syringes and injected directly onto the GC column.

Analysis of pore water from Holyhead harbour sediments.

Dissolved organic carbon. (DOC). The method of Collins and Williams (1977) was used.

Volatile organic carbon (VOC). VOC was determined by bubbling oxygen into 1-2 ml of pore water (pH 11) in a specially adapted cell. The stripped volatiles were oxidised to carbon dioxide whose concentration was estimated by an infra-red analyser.

Sulphate concentrations. Dissolved sulphate was determined gravimetrically as barium sulphate on 2-5 ml interstitial water samples.

Microcosm incubations. Experimental treatments of natural mixed populations of bacteria in sediment microcosms were attempted. 1 ml plastic syringes were used to take sediment from a Holyhead harbour core via the sampling ports, which were immediately transferred to an anaerobic jar containing nitrogen. On return to the laboratory, the sediment samples were transferred to 5 ml OFN flushed glass tubes fitted with gas tight stoppers. Incubation temperatures were 10°C unless otherwise indicated.
The treatments were: (1) Incubation of the microcosms at 20°C or 30°C for 24 hours. (2) Addition of acetate (2mM final concentration) or H^2/CO^2 mixture, followed by incubation for 24 hours. (3) Addition of sulphate (1mM final concentration) to tubes pretreated with acetate or H^2/CO^2, followed by incubation for 24 hours. At the end of the incubations the headspace gases were analysed for methane.

RESULTS AND DISCUSSION.

Acoustic sub-bottom profiling of Holyhead harbour indicated that sediments were

acoustically turbid throughout the inner harbour area, and as far as the dredged channel (Fig 3). The core samples were found to contain up to 2000 μmoles kg^{-1} of methane (Fig 4). An overall trend of increasing methane concentration with depth was noticeable, as was a trend towards higher concentrations and steeper initial concentration gradients of methane with depth for cores taken where the acoustically turbid layer approached the sediment surface (positions 6, 7 and 8 of Fig 3). The acoustic turbidity was usually between 1 m and 4 m below the sediment surface.

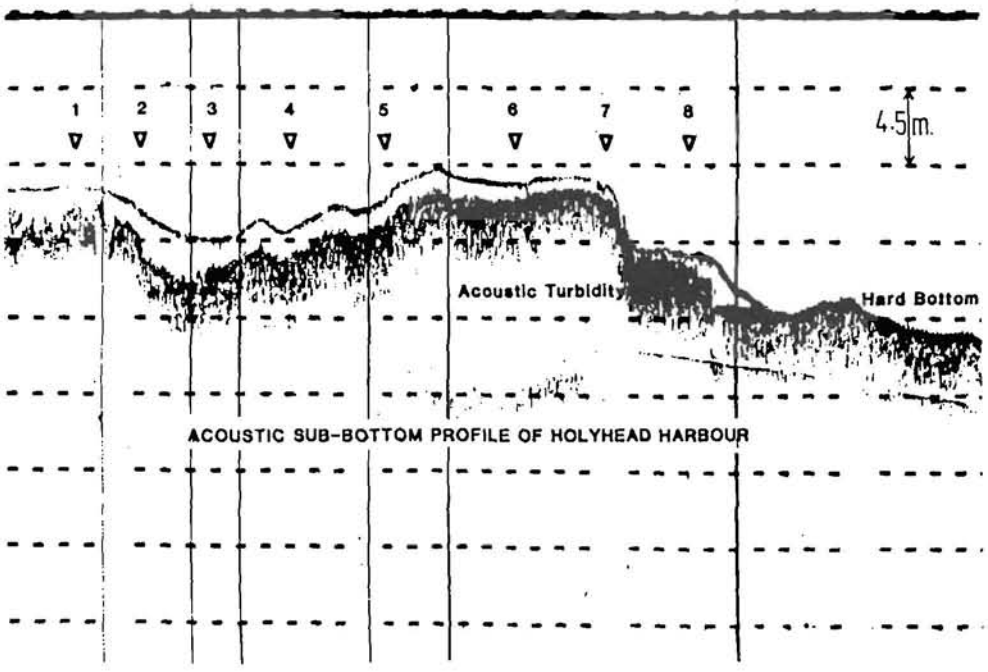

Figure 3 : Acoustic sub-bottom profiling of Holyhead harbour.

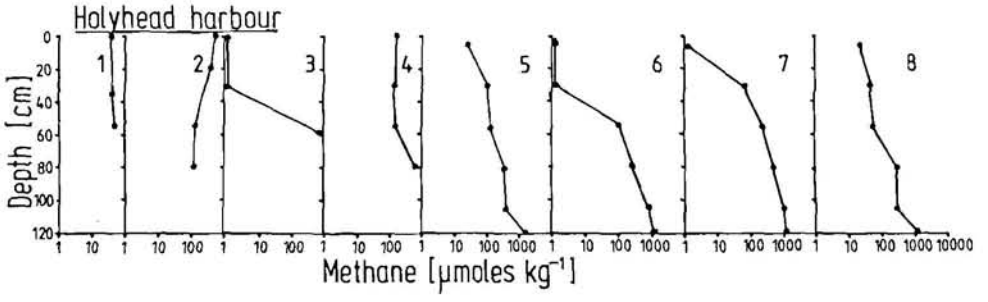

Figure 4 : Methane concentrations within Holyhead harbour sediments for sampling stations 1 to 8.

Analysis of dissolved methane concentrations for three cores taken from position A (Fig 1) shows concentration gradients similar to those demonstrated above (Fig 5). Also shown in Figure 5 are DOC, VOC and sulphate concentrations for the same cores. For the

three cores the DOC remains relatively constant throughout the column at approximately 30 mg C l^{-1}, except in one core where no DOC could be detected between 15 cm and 45 cm. Sulphate concentrations decreased down the profile to levels below 1mM at 80 cm consistent with its utilisation in the surface layers of the sediment by sulphate-reducing bacteria. In one case quantities of VOC increased down the core, indicating the production of possible substrates for the terminal bacterial processes, although the activity of these groups would normally keep the concentrations low, possibly below detection levels. The VOC was mainly being detected in the zone where sulphate levels should be sufficiently low to ensure the predominance of methanogenesis. At concentrations of sulphate above 5mM methane concentrations of less than 200 μmoles kg^{-1} were measured, but below 1mM sulphate up to 2 000 μmoles kg^{-1} (a ten-fold increase) were measured.

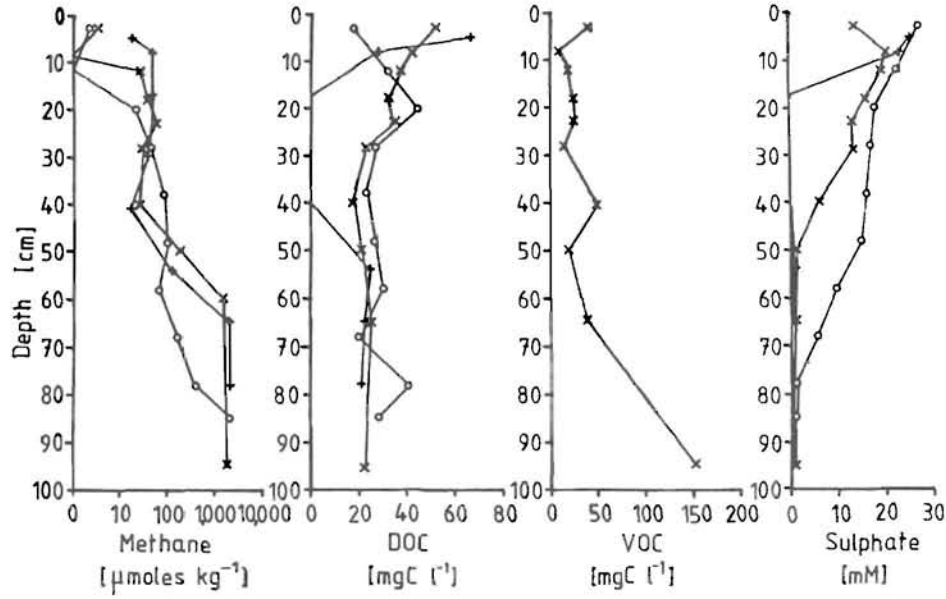

Figure 5 : Methane concentrations, DOC, VOC and sulphate concentrations for three cores from Holyhead harbour.

The results of methane analysis of Western Irish Sea cores indicated that more methane was present compared to the Holyhead harbour cores, with as much as 45000 μmoles kg^{-1} (Fig 6), but because of the increased hydrostatic pressure at 100 m compared to 10 m, these values were not unreasonably high. Gas bubble formation within the sediments is dependent upon one gas component concentration exceeding its saturation point which is itself dependent upon the hydrostatic pressure of the system (Anderson and Hampton, 1980 a). Some seasonal effect may be involved in determining the methane concentrations in the cores but insufficient data is available for that analysis. Although core blackening was a common feature of Holyhead harbour cores it was noticed in only three cores from the Western Irish sea, the same cores showed the highest levels of methane. Although we have not investigated net gas fluxes from either sediment system, bubble and pore tube formation has been noted, especially within Holyhead harbour sediments.

The Holyhead harbour microcosm experiments (Fig 7a) indicated that raised temperature stimulated methanogenesis. H_2/CO_2 was seen to stimulate methane production in

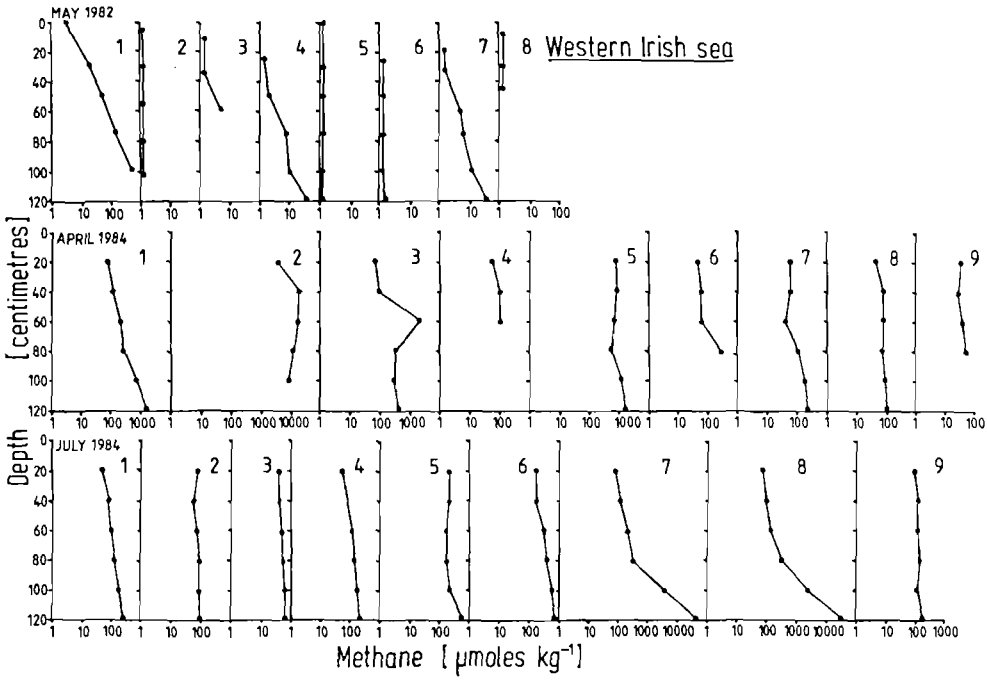

Figure 6 : Methane concentrations within Western irish sea sediments for samples collected in May 1982, April 1984 and July 1984.

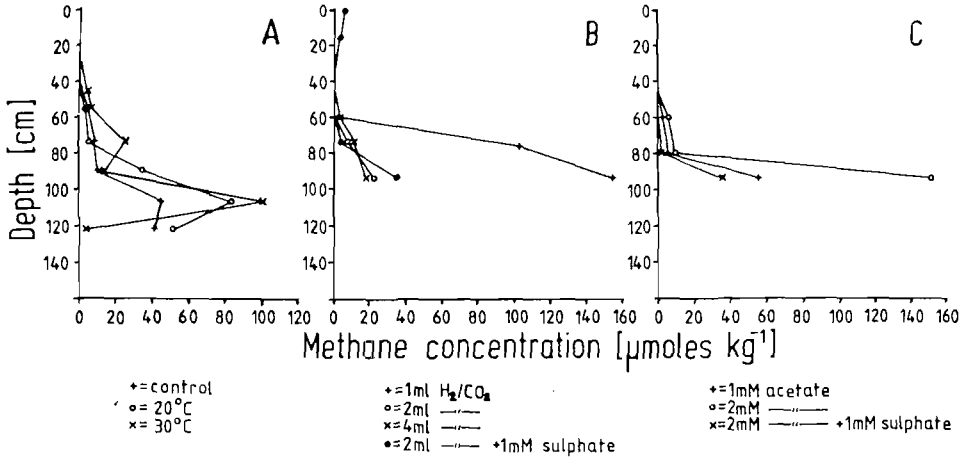

Figure 7 : Methane concentrations for microcosm experiments
A. Effect of incubation temperature.
B. Effect of H_2/CO_2 addition.
C. Effect of acetate addition.

small quantities but inhibit at high concentrations, although the addition of sulphate caused a partial reversal of this effect (Fig 7b). Figure 7c shows that acetate stimulated methane production although sulphate addition to the microcosm reduced the effect. The main conclusion was that small amounts of acetate or hydrogen and carbon dioxide

stimulated methanogenesis at depths where the sulphate levels would be expected to be at or below 1mM (Fig 5). This experiment indicated that a potential for anaerobic metabolism, and specifically methanogenesis, existed within the Holyhead harbour sediments, although we are still uncertain of the true contribution of microbial activity towards gas accumulation within such acoustically turbid sediments.

ACKNOWLEDGEMENTS.

We are grateful to the NERC for funding this work, to the officers and crew of the RV. Prince Madog for their invaluable assistance, Dr J. Bennell for practical and theoretical assistance and to Professor D. Taylor-Smith for posing the problem in the first place. A version of this paper was originally published by Crane, Russak and company in Marine Geotechnology (1986). *Vol. 6 pp* 316-332.

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