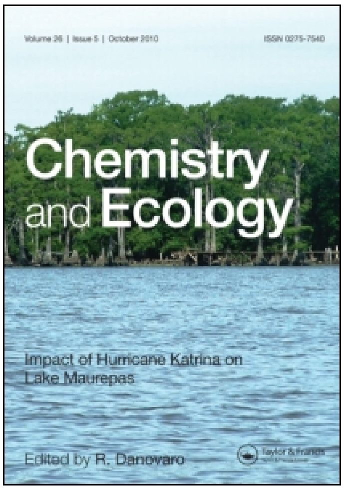

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A Comparison of Methods used for the Measurement of Organic Matter in Marine Sediment

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The content of organic matter was determined in intertidal and subtidal sediments using different methods. The methods used measured the readily oxidizable organic matter (R.O.O.M.), the loss on ignition at two temperatures, 450°C (VS_{450}) and 600°C (VS_{600}), and the fraction oxidized by hydrogen peroxide (P.D.F.). The methods removed progressively more organic matter from a given sediment in the order R.O.O.M. < P.D.F. < VS_{450} < VS_{600}. The differences between the values obtained by each method varied with the content of organic matter and were greatest at the lowest concentrations of organic matter. The relative proportions of labile and refractory organic matter varied depending upon the source of the sediment.

INTRODUCTION

In marine pollution studies, organic matter is recognized along with grain size and mineralogy as an important factor which influences the content of metals and other contaminants in sediments. In the open sea the organic content of sediments is derived from the settlement of biogenic material which originates from marine primary production. The organic matter represents directly and indirectly the food of the marine benthic fauna. In low-energy marine environments close to population centres sewage and other wastes often contribute directly to the organic content of sediments. The benthic fauna in such an area may show certain well-defined responses to an abnormal increase in organic content (Pearson and Rosenberg, 1978). The common methods used for measuring the content of organic matter in marine sediments which are not contaminated by coal (see Buchanan and Longbottom, 1970) include wet oxidation (e.g. Loring and Rantala, 1977) and loss of volatile material at a selected temperature (e.g. Rees, 1973). McCave (1979) measured the organic content of suspended sediments in coastal waters by oxidising the samples with excess hydrogen peroxide. During the course of benthic investigations in the coastal waters of Northern Ireland each of these three methods has been used on sediments from a variety of sources. The results are evaluated here with special reference to the relationship between the methods.

METHODS AND MATERIALS

Samples

Duplicate samples of sediment were collected from 41 subtidal sites on Belfast Lough (for site locations see Parker, 1982) using a benthic grab. A core of dimensions 5 cm deep by 3.7 cm diameter was withdrawn from the undisturbed sample by means of a plastic corer.

Using a similar corer a number of samples were collected from 5 intertidal sites in the Foyle estuary (for locations see Department of Agriculture, 1978). Samples were collected also from an exposed sandy beach at Portstewart (Irish Grid ref. C 810 373). A sample of mixed primary and secondary sewage sludge was obtained from Coleraine sewage works. Only the particle size fraction < 210 μm was used in the organic matter determinations. This fraction was separated from the coarser particles by washing through a nylon sieve of the appropriate mesh size using distilled water. The fine material was collected in an evaporating basin and allowed to settle overnight. The excess water was poured off and the sediment was oven dried at 105°C for 24 h. It was then crushed using a mortar and pestle and stored in air-tight glass containers until required for analysis.

Wet oxidation

This method followed the detailed description given by Loring and Rantala (1977). About 0.5 g of the prepared sediment was treated with a mixture of IN $K_2Cr_2O_7$ and concentrated H_2SO_4. No external heat was applied and the reaction time was 30 min. After this time the excess dichromate was titrated with 0.5 N ferrous ammonium sulphate solution. From the result of the titration the organic content was calculated using the equations provided. This component is referred to as readily oxidisable organic matter (R.O.O.M.).

Loss of volatile solids

Routinely the weight loss from sediment samples was measured at 2 temperatures in the following way. About 5 g of the prepared sediment was treated with an excess of 10% hydrochloric acid in order to remove the carbonates which may interfere with the determination (Buchanan, 1971). The mixture was then filtered using a glass fibre filter and dried at 105°C. The dry sediment was crushed using a mortar and pestle and about 1–2 g was weighed into a silica crucible. This was heated in a muffle furnace for 1 h at 450°C then cooled and reweighed. It was further heated for 1 h at 600°C and reweighed. The weight losses at 450°C and 600°C were calculated and they are referred to as VS_{450} and VS_{600} respectively. In addition selected samples of sediment, plus a sample of sewage sludge were dried at 100°C and heated for 1 h at 100°C increments of temperature up to a maximum of 600°C, and the weight loss over each interval was determined.

Hydrogen peroxide method

A selection of samples from the Foyle estuary was treated by this method which was adapted from the method of McCave (1979). A weighed amount (*c*1 g) of the prepared sediment was placed in a glass dish and covered with 6% H_2O_2. The dish was kept overnight in an oven at 60°C. The peroxide was then evaporated to dryness at 105°C. The dish was reweighed and the weight loss recorded as the peroxide degradable fraction (P.D.F.).

RESULTS

Table I compares the means, standard deviations and range of values of organic matter of samples from Belfast Lough. The sediments varied from organic rich muds associated with the docks, to clean shelly sands occurring at the mouth of the lough. The methods of R.O.O.M., VS_{450} and VS_{600} in that order removed progressively more organic matter from the sediment samples. The relative difference between the methods was greater at the lower levels of organic matter. The lowest levels of organic matter in Belfast Lough (Table I) were of similar order to those measured in the sediment of Portstewart beach. Here the mean values for triplicate samples were 0.08%, 0.24% and 0.32% for R.O.O.M., VS_{450} and VS_{600}, respectively. The relationship between the values of P.D.F. and VS_{450} is shown for Foyle estuary samples in Table II; the relative difference was again slightly greater at the lower level of organic matter. In a linear regression the values of R.O.O.M., VS_{450} and VS_{600} were very highly significantly correlated with each other ($p < 0.001$). Similarly, there was a high degree of correlation between P.D.F. and VS_{450} but slightly less of the variance was explained by this regression (Table III).

TABLE I

Percentage of organic matter in duplicate samples from 41 subtidal sites in Belfast Lough

Method	Mean ± S.D.	Minimum	Maximum
R.O.O.M.	1.69 ± 2.15	0.09	12.22
VS_{450}	2.91 ± 2.92	0.04	16.61
VS_{600}	3.63 ± 3.19	0.62	18.02

TABLE II

Percentage organic matter in 20 samples from 5 intertidal sites in the Foyle estuary

Method	Mean ± S.D.	Minimum	Maximum
VS_{450}	4.99 ± 2.50	1.96	9.31
P.D.F.	3.97 ± 2.00	1.24	8.50

TABLE III

The percentage of variance explained by the regression of different combinations of organic analysis of Foyle estuary (a) and Belfast Lough sediments

	R.O.O.M.	VS_{450}	P.D.F.
VS_{450}	98.0%	—	82.6%[a]
VS_{600}	96.6%	99.4% 99.2%[a]	87.4%

Figure 1 compares the loss of volatile solids over a range of temperatures for Belfast Lough and Foyle estuary sediments and for a sample of sewage sludge. The latter showed a progressive decrease in the percentage weight loss over successive temperature intervals; over 46% of the volatile material was driven off at 100–200°C whilst only 0.7% was removed between 500–600°C. In Belfast Lough, site B22 in the docks contained anaerobic mud and did not support a benthic fauna. The largest weight loss in these samples occurred between 200–300°C and the least between 500–600°C. At site B18, an adjacent site in the docks area, the fauna was dominated by

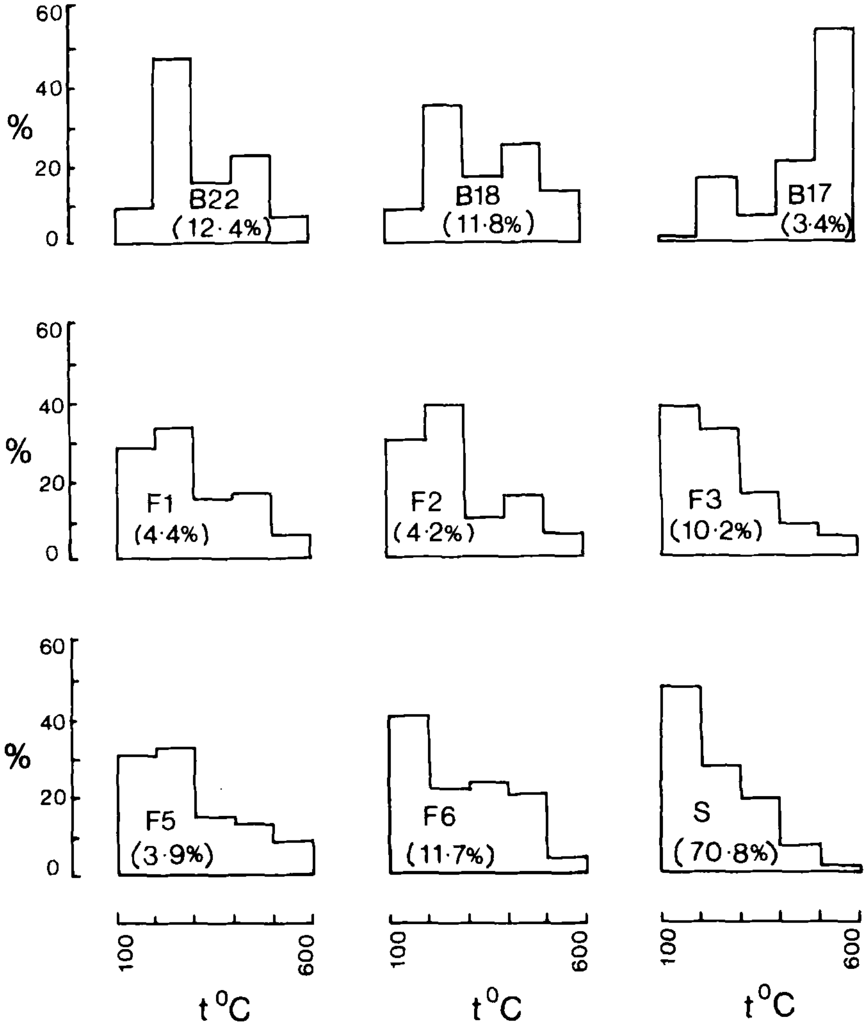

FIGURE 1 The loss of volatile solids from samples of Belfast Lough sediment (B), Foyle estuary sediment (F) and sewage sludge (S) at increments of 100°C; loss over each increment is expressed as a percentage of VS_{600}. The value of VS_{600} for each sample is shown in brackets.

oligochaetes and small polychaetes, although conditions were strongly reducing below the surface of the sediment. The total organic content and the pattern of weight loss at increasing temperatures were similar at both of these sites. Samples of aerobic sand from site B17 which was located in the outer Lough showed a different pattern of weight loss. The dominant volatile fraction was removed in the temperature range 500–600°C and comprised 54% of the total volatile material. The sediments from the Foyle estuary were of two types. Sites F3 and F6 were close to sewage effluent outfalls which had visible effects on the local shoreline; both sites had organic contents of > 10% and the infauna was sparse. The remaining Foyle sites contained about 4% organic matter and contained high numbers of estuarine invertebrates dominated by *Corophium volutator* (Pennant), *Hydrobia ulvae* (Pallas), *Manayunkia aestuarina* (Bourne) and Oligochaeta. Samples from sites F3 and F6 showed the maximum loss at 100–200°C whilst the remaining sites had a maximum loss between 200–300°C.

DISCUSSION

In previous studies a variety of methods have been used in order to assess the organic content of marine sediment. The present work shows that each of the commonly used methods may provide an adequate assessment of the relative content of sedimentary organic matter. However, there are important limitations regarding the comparability of studies which have employed different methods. Notably, there is no simple factor for converting values derived from one method for comparison with values obtained by other methods. This is especially true when the sediments examined contain a wide range of organic matter contents, for the differences between methods vary with the organic content. For example, the VS_{450} values varied between 4.4× and 1.4× greater than the values of R.O.O.M. at the minimum and maximum levels respectively of organic matter in Belfast Lough sediments. Comparisons made between studies carried out by loss on ignition at different temperatures may be misleading as the proportions of material driven off at different temperatures may vary with the source of the organic matter. Thus in studies of the organic content of Liverpool Bay, loss on ignition was carried out at 450°C (Rees, 1973), 500°C (Winter and Barrett, 1972), 600°C (Crickmore and Kiff, 1972) and 700°C (Gould, 1976) resulting in a lack of comparability between the results.

Many authors have described the changes in the nature of organic matter which may take place in the sea. McCave (1979) showed that suspended particulate matter in nearshore waters may contain over 30% P.D.F. at the sea surface, whilst particles near the sea bottom contained between 14–16% P.D.F.; this was attributed to the gradual decomposition of organic matter settling through the water column. The organic levels in sediments in the open sea are of the order of 0.2% whilst in coastal waters sediments contain

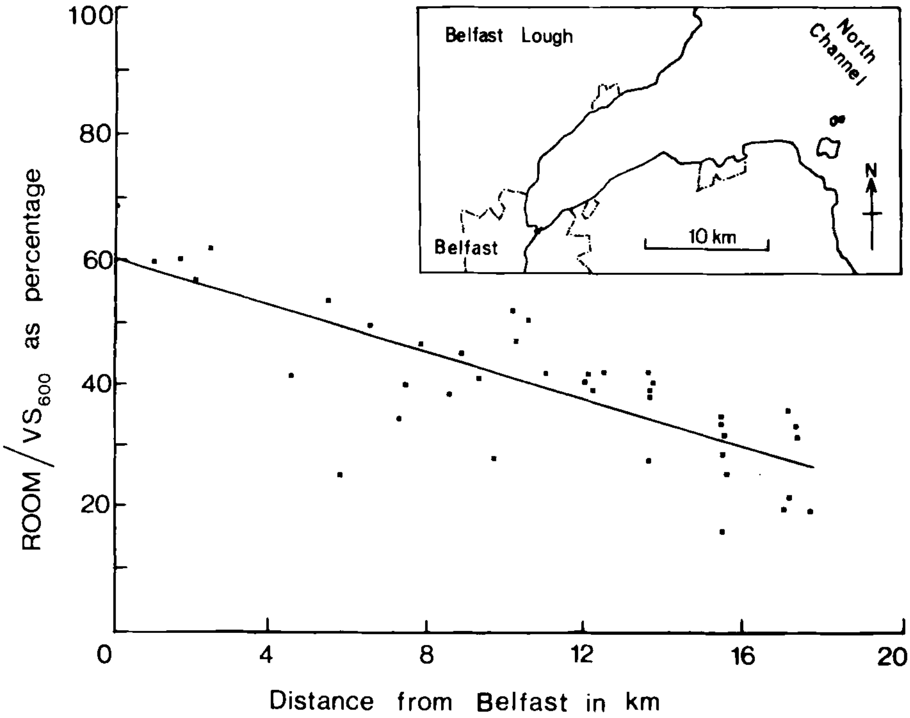

FIGURE 2 The variation in the ratio of labile (R.O.O.M.) to total (VS$_{600}$) organic matter with increasing distance from Belfast. Correlation coefficient from the regression line = −0.78.

on average between 1% and 5% of organic material, according to Degens and Mopper (1976). These authors pointed out that the organic matter in sediments became increasingly more refractory in nature with increasing depth of the overlying water column, suggesting that the more labile components were preferentially mineralized. Degens and Mopper (*op. cit.*) examined changes in the nature of sewage sludge and verified that the process of microbial decomposition caused a gradual increase in the relative amount of refractory organic material present. Freshly-collected sewage sludge may contain comparatively small quantities of refractory organic matter (Figure 1). It follows that marine sediments which receive relatively fresh inputs of solids derived from sewage should show different characteristics in their organic matter to sediments which are distant from such inputs. A substantial amount of organic-rich particulate material may enter the docks and inner areas of Belfast Lough from direct inputs of sewage effluent and via storm-water overflows (Parker *et al.*, 1979). The deeper waters of the outer lough are influenced by the strong currents of the

North Channel and organic inputs to the sea bed can be expected to be less, and to be of a more refractory nature than in the inner reaches. The distribution of organic matter in the lough (Parker, 1982) verified that levels were highest in the docks area and decreased with increasing distance seawards. Figure 2 shows the change in the ratio of labile (R.O.O.M.) to total (VS_{600}) organic matter which occurred within the lough and verified that there was a progressive decrease in the relative importance of labile substances with increasing distance from Belfast. Thus the composition of the organic matter did appear to change in relation to the amount deposited in the sediment. In the docks area where the deposition of organic matter was greatest the labile fraction driven off at temperatures between 200- 300°C was dominant. In contrast, sites at the outer reaches, exemplified by site B17 (Figure 1) were dominated by more refractory components. The Foyle estuary sediments contained high amounts of the more labile fractions at all sites but here, in contrast to Belfast docks, the fraction lost at temperatures of 100–200°C was relatively high. The reason for this difference is not clear but may reflect differences in the types and rates of input and in the decomposition processes which occur in these areas. Degens and Mopper (1976) emphasized the importance of the sediment-dwelling fauna in promoting the decomposition of organic matter. Comparing the organic matter of the two sites in Belfast docks, there appeared to be little difference in the characteristics of the organic matter although only one of the sites contained benthic fauna. However, it is probable that the important biological processes may occur only in the upper few centimetres under these circumstances and more detailed measurements than were made here would be required to elucidate the influence of the fauna on the nature of the organic matter. Similarly, preliminary observations on the Foyle sediments suggested that the density of intertidal animals did not make a great deal of difference to the relative proportions of labile and refractory organic matter. Again, more detailed measurements may be needed to validate this finding.

In conclusion, the methods examined here may all give satisfactory estimates of the organic content of marine sediments. However, even within small sea areas the characteristics of the organic matter may change; this precludes the use of a simple conversion factor in order to compare values obtained by different methods. The differences between values obtained by the different methods may be especially great at low organic levels.

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