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DETERMINATION OF METAL CONTENT OF SEDIMENTS IN RELATION TO DUMPING AND DISCHARGE CONTROL

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INTRODUCTION

Of the various wastes which are dumped at sea at the present time, sewage sludge and dredging spoil account for by far the largest quantities. Results reported at the 62nd Statutory meeting (Portmann, 1974) showed that these two materials can contain quite high concentrations of a number of heavy metals. As a result relatively large quantities of these metals may be introduced into defined dumping areas. Since it is known that many marine organisms can accumulate heavy metals to such an extent that the accumulated concentration may be harmful either to the animal or to its predators, including man, it is essential that the concentration of metals in the sediments be kept under observation in order to ensure that no unacceptable increase occurs.

Analysis of sediments for metals poses certain difficulties and this paper summarises some of the work which has been done in order to establish a method which will give reasonably consistent and reliable results on any sediment sample.

For the purposes of dumping or discharge control, the ideal analytical procedure should measure only that portion of the metal in the sediment which was introduced, as a result of man's activities. Since sediments also contain metals of minerological origin, it is difficult to separate these two components. Although there are several methods for extracting only the lightly attached metal (Chester and Hughes, 1967; Carmody et al., 1973) it was considered that there was inadequate information to show whether these methods would measure all or part of the 'pollutant metal' and the "natural metal". It was therefore decided to adopt a fairly rigorous extraction procedure which would certainly extract all the 'pollutant metal', but which would stop short of complete dissolution of the entire sediment and consequent complete extraction of the "natural metals."

Earlier work at Burnham-on-Crouch had used concentrated nitric acid as an extractant and analysis of either whole sediment samples or separate size fractions. However, whole sediment analysis posed severe sub-sampling problems and analysis of many separate size fractions of each sediment sample is extremely time consuming. It was therefore decided to investigate the distribution of metals in different fractions, and to examine the possibility of reducing routine analysis to one or two fractions.

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ANALYTICAL METHODS

A variety of extraction procedures was used to extract the metals, other than mercury, from the sediments, but throughout the work the methods of final determination were the same. Mercury was always analysed according to the standard procedure outlined below. All water used was doubly distilled from borosilicate glass and all the reagents were of 'Analar' grade, except nitric acid which was redistilled from technical grade bulk supply.

Mercury determination: Samples of sediment (4g) were digested in open flasks with 10 ml of concentrated nitric acid with 10 ml concentrated sulphuric acid and in the presence of potassium persulphate. The temperature was slowly raised to at least 150-170^{o}C. After cooling the samples were reduced with stannous chloride and mercury vapour was analysed by flameless AAS at 253.7 nm.

Determination of other metals: Lead, zinc, chromium, copper and cadmium were determined on approximately 3g samples of sediment. After digestion on a hot plate the samples were cooled and filtered through prewashed Whatman No. 50 filter papers (later centrifuged) and the filtrate made up to volume in 50 ml volumetric flasks. Samples were measured against freshly prepared working solutions using a Perkin-Elmer 306 AAS instrument and a standard air-acetylene flame. Background correction was found to be necessary and was always used in the determination of lead and cadmium.

EXTRACTION PROCEDURE

As mentioned earlier, one objective of this work was to devise a method which would determine all the free and surface bound metal which could conceivably have been derived from pollution, without necessarily extracting metal bound in the mineral structure of the sediment particles. Since some of the metal is likely to be associated with organic matter, it was considered essential that this be decomposed. With this in mind, nitric acid in one of a number of strengths and for various periods or in admixture with prechloric acid appeared to offer the best possibility of complete extraction.

Several procedures were tried using a sandy-silt type of sediment and the results are given in Table 1. These indicated that a digestion period of 6 hours was needed in order to extract all the metals. There was no significant difference in efficiency of extraction when perchloric acid was included with the nitric acid and, since the inclusion of perchloric acid posed a number of practical problems, its use was not adopted. There was also no significant difference between the results obtained using 10 ml of concentrated nitric acid and 20 ml of 5M nitric acid. The latter digestion solution showed no tendency to 'bump' whereas the former did, occasionally with loss of part of the sample: 5M nitric acid was therefore adopted as the extraction solution for all future work.

LOCATION OF THE METAL IN THE SEDIMENT

Most of the results in the literature indicate that the bulk of the metal in a sediment is likely to be associated with the fine fraction, indicating that the coarse part of a sediment could be rejected in an investigation of this nature. This was, however, investigated under our conditions using three different sediment types, all from relatively polluted situations: (a) a sandy-gravel (b) a sandy-silt (c) a silt-clay; sediments a and b came from areas in which wastes are dumped.

Each of these sediments was wet sieved into separate particle size fractions and each of these fractions was analysed using the 20ml 5M nitric acid extraction system described above. The results of these analyses are shown in Table 2, 3 and 4. The two finer sediments were also analysed without fractionation but this was impossible with the coarser material owing to the difficulty of obtaining a reasonably consistent sample. As expected, the results show that the highest concentrations of metal are to be found in the fraction of less than 63 μm size. However, there appear to be significant concentrations of at least some metals in larger particle size fractions eg. 17 μg/g copper in the 0.50-0.25mm fraction and 32 μg/g of zinc in the 2-1mm fraction of the sandy-gravel; 74 μg/g lead in the 0.125-0.063mm fraction of the sandy-silt.

Figure 1 shows the relative amounts of the particle size fractions in the three sediment types and indicates that, even though there may be some metal in the coarser fractions, in most cases the contribution this makes to the total metal is negligible compared to the proportion in the finer fraction.

Analysis of separate particle size fractions is time-consuming. For the purposes of dumping or discharge control the particle size fraction with which the metal is associated is not important. The analytical work load can be reduced by analysis of only the finer fractions of the sediment since it has been shown the coarse component does not contain a significant proportion of the total metal. More sample is likely to have to be sieved to obtain an adequate amount of finer fractions, and therefore the sieving process becomes more time-consuming the smaller the fraction required. It is therefore desirable to select a cut-off point which is as large as possible so as to (a) retain the maximum quantity of metal which could conceivably be of pollutant origin (b) reduce sieving to a minimum. At the same time analytical precision must not be sacrificed due to inconsistencies in sampling.

Experiments were therefore undertaken to establish a suitable sieving cut off point. For this purpose two well mixed sediments were used: they were analysed as follows:-

(i) all that which passed a 2 mm sieve
(ii) all that which passed a 0.5 mm sieve
(iii) all that which passed a 0.090 mm sieve
(iv) all that which passed a 0.063 mm sieve.

The 0.090 mm sieve was selected because this size approximates to the maximum size attained by naturally occurring floccules of silt-clay/organic matter.

Each fraction was sub-sampled at least six times and each sub-sample was analysed separately. The results are shown in Table 5. These indicate that there is little variation in metal content analysed in samples of less than 90 µm and that highest concentrations are to be found in the particle size fractions of less than 90 µm, thus confirming the earlier conclusion. Therefore in order to obtain reasonable sub-sampling precision, the particle-sizes above 90 µm (0.090 mm) must be rejected. However, some dumped material contains particles of up to 0.5 mm size and it is therefore desirable that additionally the fraction 90 µm - 500 µm is analysed, even though reproducibility will not be so good in some cases.

STORAGE OF SAMPLE MATERIAL

It is rarely practicable to analyse all samples from a survey immediately after collection and storage for at least a limited period is usually necessary. Most sediments contain a significant amount of organic material (see Tables 2-4). It is also known that much of the metal is associated with this organic fraction (Andrulewicz, 1975, Ollavsson, 1970). During storage under normal laboratory conditions, even in sealed containers, this organic material will decompose and investigations were therefore conducted to examine whether such decomposition affected the metal content and if so which storage system could be used to minimise such changes.

Samples were stored over a period of approximately three months under refrigeration at -18°C, under formalin at room temperature, and without preservative at room temperature respectively. Sub-samples were taken and analysed at intervals of approximately 1 month. The results of analyses of these successive analyses were not conclusive, although they suggest that there is no change in metal content, even of mercury, over a 4 month period with or without attempts at sample preservation. However, the organic content of the test samples was low and it is likely that charges would occur in samples with a higher organic content. It is therefore suggested that analysis should be conducted as soon as possible after collection.

CONCLUSIONS

For the purpose of routine monitoring of metal levels in sediments in areas subject to input of metals by either dumping or discharge, work to date suggests that no preservation of sediment samples is necessary between collection and analysis over a period of at least 3 months. However, the general validity of this conclusion is still being examined. The metal of interest lies mainly in the finer fraction of the sediment and analysis can conveniently be accomplished by sieving the sample through a 0.090 mm seive and analysing sub-samples of that portion which passes through the sieve. Digestion with 20 ml of 5M nitric acid affords an adequate method of extraction for the metals of interest, other than mercury for which 10 ml each of concentrated nitric and concentrated sulphuric acid are required.

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TABLE 1

Results of extraction of metals using different extraction procedures

Procedure	Zn μg/g	σrel.	Cu μg/g	σrel.	Cr μg/g	σrel.
10 ml HNO_3 Conc., 1 h	34.8	2%	8.67	4%	8.67	2%
10 ml HNO_3 Conc., 3 h	36.1	2%	8.36	5%	9.93	4%
10 ml HNO_3 Conc., 6 h	38.2	4%	8.54	4%	13.39	10%
20 ml HNO_3 5M, 6 h	41.9	5%	9.16	6%	17.70	8%
20 ml of 3:1 HNO_3 $HClO_4$ 6 h	38.5	1%	9.10	6%	17.65	2%

σ rel. = standard deviation as % of mean

TABLE 2

Distribution of various analytes in sandy gravel sediment

Size Fraction mm	Org. Mat.	Hg tot. μg/g	σrel.	Pb μg/g	σrel.	Zn μg/g	σrel.	Cu μg/g	σrel.	Cr μg/g	σrel.	Cd μg/g
4.00 - 2.00	1.87	0.03	<1%	15	3%	32	8%	16	9%	7	9%	<0.5
2.00 - 1.00	2.12	0.04	10%	11	5%	32	9%	7	7%	9	5%	<0.5
1.00 - 0.50	1.51	0.02	<1%	10	5%	24	4%	6	10%	6	9%	<0.5
0.50 - 0.25	1.30	0.02	<1%	17	9%	26	9%	17	7%	6	1%	<0.5
0.25 - 0.125	1.01	0.04	<1%	12	10%	19	7%	5	11%	5	11%	<0.5
0.125 - 0.063	0.87	0.03	10%	21	5%	24	6%	5	11%	6	10%	<0.5
<0.063	11.66	0.40	4%	210	5%	183	2%	43	7%	40	6%	<0.5

σrel. = standard deviation as % of mean.

TABLE 3

Distribution of various analytes in sandy silt sediment

Size Fraction mm	Org. Mat. %	Hg tot µg/g	σrel.	Pb µg/g	σrel.	Zn µg/g	σrel.	Cu µg/g	σrel.	Cr µg/g	σrel.	Cd µg/g
Without fractionation	4.88	0.35	8%	66.9	2%	87.6	2%	19.3	2%	25.2	8%	<0.2
0.50 - 0.25	1.63	0.07	<1%	12.5	10%	46.5	1%	3.6	8%	7.2	2%	<0.2
0.25 - 0.125	1.39	0.06	<1%	14.5	4%	47.2	2%	3.2	5%	8.5	5%	<0.2
0.125 - 0.063	1.71	0.12	8%	74.4	6%	78.0	1%	25.9	6%	27.5	6%	<0.2
<0.063	9.84	0.95	2%	193.0	3%	165.7	6%	64.0	4%	46.0	3%	<0.2

σ rel. = standard deviation as % of mean

TABLE 4

Distribution of various analytes in a silt-clay sediment

Size Fraction mm	Org. Mat. %	Hg tot µg/g	Pb µg/g	Zn µg/g	Cu µg/g	Cr µg/g	Cd µg/g
Without fractionation	9.3	0.32	50.0	80.0	18.0	38.0	<3
0.125 - 0.063	4.4	0.33	27.6	33.7	7.4	13.1	<3
<0.063	10.6	0.43	80.7	106.8	25.0	57.1	<3

σrel. = <10% in all cases

TABLE 5

Distribution of various analytes in sediment A and sediment B

A

Size Fraction mm	Hg tot μg/g	σrel.	Pb μg/g	σrel.	Zn μg/g	σrel.	Cu μg/g	σrel.	Cr μg/g	σrel.
<2.00	0.11	9%	37.9	2%	68.6	3%	14.4	7%	21.4	5%
<0.50	0.13	8%	60.5	6%	110.2	4%	14.8	3%	24.0	4%
<0.090	0.23	9%	115.5	2%	194.1	2%	27.7	2%	48.7	5%
<0.063	0.23	9%	95.2	1%	157.9	3%	31.5	4%	55.4	5%

B

<2.00	0.11	33%	46.8	35%	33.4	12%	27.0	38%	15.3	11%
<0.50	0.26	15%	43.0	16%	56.5	5%	18.3	21%	19.2	8%
<0.90	0.32	3%	37.7	4%	53.8	6%	13.5	5%	21.5	5%
<0.063	0.43	2%	68.3	2%	91.5	3%	27.9	5%	38.8	4%

σ rel. = standard deviation as a % of the mean

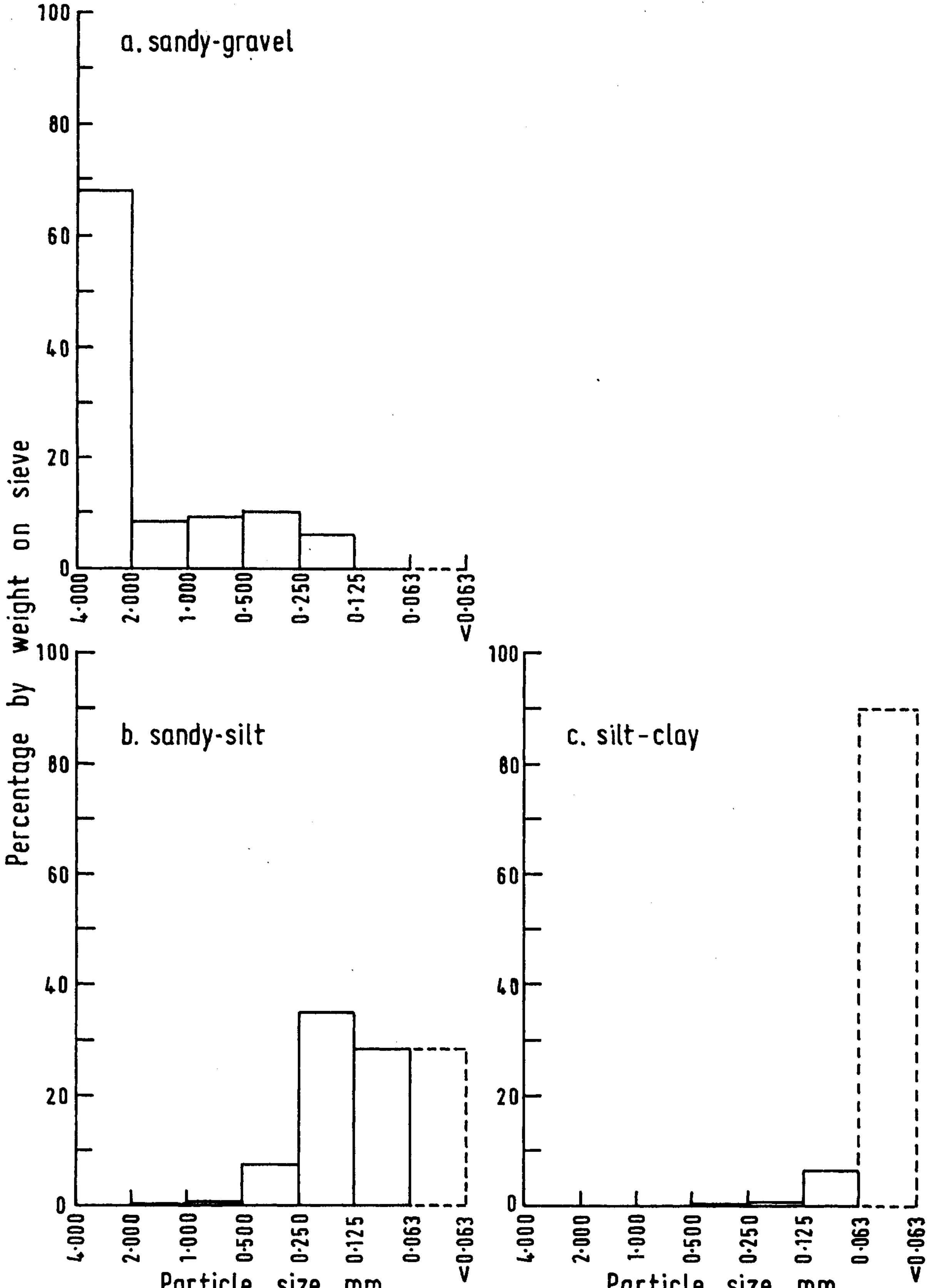

Figure 1. Particle size distribution of sediments