International Council for the Exploration of the Sea

CM 1991/E:12
Marine Environmental Quality Committee

SAMPLING STRATEGY TO DETECT A CHANGE IN CONCENTRATION OF TRACE ORGANIC CONTAMINANTS IN MARINE SEDIMENT

by

A G Kelly, D E Wells and R J Fryer

SOAFD Marine Laboratory
PO Box 101, Victoria Road
Aberdeen AB9 8DB
Scotland, UK

SUMMARY

The ability to detect changes in the environmental level of contaminants depends on the variances associated with the measurements. The sources of variance contributing to the determination of chlorobiphenyls and organochlorine pesticides in sediment from the Garroch Head sewage sludge disposal site have been examined. The total variance is considered to be the sum of a "field variance" associated with this site, and long term analytical variance. The significance of these sources of variance for sampling strategy and achievable precision are discussed.

1. INTRODUCTION

Sediment can be a sensitive indicator for both spatial and temporal trend monitoring of trace organic contaminants in the marine environment. Many environmentally important organochlorine contaminants are firmly bound to the organic layer in sediment, and particulate material suspended in the water column with a high sediment:water partition coefficients (10^5 to 10^7). Sediment is therefore a major environmental sink for contaminants such as the chlorobiphenyls, organochlorine pesticides, and polychlorodibenzo-*p*-dioxins and furans and can be more representative of the particular locality than the water or biota. Sediment tends to be less useful for monitoring more water soluble contaminants like chlorophenols and lindane, where a substantial fraction of the total aquatic load remains in the dissolved phase.

The value of sediment as a monitoring tool is critically dependent on the local seabed environment. Only in those areas where sedimentary accumulation is not subjected to extensive mixing by hydrographic events, bioturbation or dredging, will a record be preserved of the long term input of contaminants. Given such an environment, the depositional rate will determine the minimum frequency of monitoring.

minimum sampling rate = sampling depth (cms)/deposition rate (cms/year)

In reality this rate will require modification to take account of estimated mixing rates in the sediment (Larsen and Jensen, 1989).

Sedimentation rates in coastal mud basins have been estimated to be between 0.5-1.5 mms/year (Pheiffer Madsen and Larsen, 1986) and 3 mms/year (Baxter, Stenhouse and Drndarski, 1980). Such areas will provide information on input integrated over several years. High deposition environments such as tidal flats, estuaries or accumulating dump grounds can be monitored annually to determine the effect of changes in input. Such conditions apply to the Garroch Head sewage disposal site in the Clyde estuary, west Scotland (Fig. 1). This is an accumulating site (MacKay, 1986) with an annual deposition rate of 1.4 cm/year (A G Kelly, unpublished data). This site has particular interest since the sludge disposal is due to terminate in 1998 in line with current UK government policy to cease sea disposal of domestic wastes. This change in input should lead to a decline in the levels of sediment bound organochlorine contaminants at Garroch Head and can be monitored to provide information on the eventual fate of OC contaminants, and permit assessment of the long term impact of the sludge dumping on the local marine environment.

One aim of several marine monitoring programmes for the North Sea is to assess any temporal trends in marine matrices; eg "Purpose 3" of the ICES monitoring programme (ICES, 1984) and "Purpose D" of the Joint Monitoring Programme of OSPARCOM (OSPARCOM, 1990). The North Sea Task Force (NSTF) plan to assess the feasibility of temporal trend monitoring in 1993, in the light of data returned for the 3rd Quality Status Report of the North Sea (NSTF, 1990) and an initial assessment by ICES, of trend monitoring data for contaminants in fish muscle has been recently completed (ICES, 1989a).

The Precision of Contaminant Measurements

The success of any monitoring programme in achieving its desired aims is dependent on the assessment of the long term variance associated with the measurements which are made. This variance must be known in order to determine whether any observed long term changes in contaminant concentration are the result of chance or are indeed statistically significant (ICES, 1989b).

All sources of variance contributing to a measurement must be considered when assessing its overall precision. The total variance of measurements of chemical parameters in environmental matrices is the sum of the individual variances associated with sampling (σ^2_s), analysis (σ^2_a) and the inherent variability of the sample population under study (σ^2_p), ie

$$\sigma^2 = \sigma^2_s + \sigma^2_a + \sigma^2_p$$

The contribution of population variance can be reduced by normalising chemical measurements with respect to known variables. In fish, specific sampling guidelines have been developed to enable normalisation with respect to sex, length and lipid content (ICES, 1990a). For sediment, both particle size fractionation into a <63 μm fraction, and measurement of organic carbon content have been suggested as means of normalising grossly differing sediment types (ICES, 1989b). This approach has found application when comparing sediment from diverse locations (eg Lohse, 1988).

A sediment "population" variance can result from minor topographical variations in the sea bed, localised current movements, varying population density of benthic biota and those factors which effect deposition and mixing rates. However, in practice a sample population variance cannot be isolated from the sampling variance.

In the case of sediment, the accuracy of placement of a ship-deployed grab or core sampler is at best 10-50 m using modern navigational techniques. Replicate sampling within such an area is not possible in routine operation. The population and sampling variance must, therefore, be combined as a " field" variance (σ^2_f). This field variance has been estimated in the determination of heavy metal concentrations for replicate analysis of sediment (Krumgalz *et al.*, 1989). Substantial field variations for sediment bound organic contaminants have been demonstrated in a survey of total hydrocarbon in sediment around two North Sea oil rigs. At sampling stations varying from 250-5,000 m distance a mean coefficient of variation (CV) of 45% was found at rig "A" (20 stations) and 44% at rig "B" (nine stations). The CV of the analytical method was 3% (Howells *et al.*, 1989).

A reasonable initial estimate of the field variance can be obtained through a pilot study of multiple samples and multiple analyses of these samples at the site of interest.

The short term analytical variance is often but incorrectly, used in developing protocols for monitoring programmes. This is readily determined with little effort, but only reflects the current analytical precision and is an underestimate of the true analytical precision (Wells and Kelly, in press). A better estimate of the long term analytical precision may be accomplished as part of an ongoing quality control procedure based on the periodic analysis of laboratory reference materials (Wells, 1988) and the occasional analysis of certified reference materials to assess bias. Certified reference materials for chlorobiphenyls (CBs) in sediment and sludge are available from the Community Bureau of Reference (BCR) of the European Community and from the National Research Council of Canada (NRCC). A compilation of reference materials for use in marine science is available (Cantillo, 1989).

In this paper the ongoing laboratory quality control data and specific sampling at Garroch Head has been used to derive estimates of both the mean levels of persistent organochlorine contaminants in sediment at the site and the analytical and field variances associated with such measurements. These data have been used to estimate the critical rejection value in a "t-test" to detect a decrease in the mean sediment contaminant concentration. The relationship between various sampling and analytical schemes and this critical value has been explored.

2. EXPERIMENTAL

Sediment samples were collected by FRV *Scotia* at Garroch Head (Fig. 1) within the area licensed for disposal of sewage sludge, a circle of radius 0.5 nautical miles centred on 55°38.48'N, 05°00.48'W, in a water depth of 70 m. Cores were obtained with a Craib corer (Craib, 1965), designed to minimise disturbance of the surface sediment by "soft" landing the corer body and hydraulically damping penetration of the core tube into the sediment. Five replicate cores were taken.

The cores were sectioned into 5 cm slices and frozen at -20°C. After freeze-drying and homogenisation, a subsample of the sediment was extracted in a soxhlet for four hours using dichloromethane. The extract was concentrated, cleaned-up, and separated into two fractions, one containing predominantly CBs, and the other organochlorine pesticides. (Wells *et al.*, 1985). The internal standard was added and each fraction was analysed by GC-ECD. Peaks were quantified by a two level calibration within the linear range of the ECD detector.

3. ASSESSMENT OF VARIANCE COMPONENTS

3.1 Analytical Variance

The short term analytical variance was determined by four replicate analyses of the top (0-5 cm) slice of one core (Table 1).

The long term analytical variance was assessed by replicate analyses of a bulk sediment sample obtained from the Garroch Head site and prepared in our laboratory as a laboratory reference material (LRM) (Wells and Kelly, in press). Samples of this LRM were analysed over a 12 month period to produce the data listed in Table 1.

The little comparable data published concerning variation in trace organic analysis derives mainly from intercomparison exercises. The reported intra-laboratory "short term" variation, which is generally a reflection of the best performance of a laboratory, was 10% and 3% for unspiked and spiked herring oil at 1 and 2 µg/g chlorobiphenyl concentration (Uthe and Musial, 1980). The coefficients of variation for the analysis of individual pesticides at this concentration was between 10-15% (Horowitz *et al.*, 1980). This study lead to the proposal of the "Horowitz" curve relating the CV of the method, as powers of 2 with the concentration of the determinand, expressed as powers of 10. At more typical environmental levels of 1 ng/g, the Horwitz curve would predict a value for short term variation of 40-50%. However, the Horwitz curve is only an empirical relationship based on the data from a series of intercomparisons in the 1970s and should not be regarded as a limitation on the improvement of measurement. The CV of 7-28% found in this study reflects advances in analytical methodology (eg the capillary column) and an increased awareness of the main sources of error (eg calibration solutions and instrument calibration), over the past decade. The long term analytical variation measured for sediment LRM125 is higher in every case than the short term variation (Table 1). For the chlorobiphenyls the mean ratio is a factor of 2.1. This is not unexpected as additional sources of both random error and bias are introduced to the analytical protocol on the longer timescale. Bias has been shown to be the main source of interlaboratory variation in intercomparison exercises

with interlaboratory CVs of 30-70% at the 10-100 ng/g level (Holden *et al.*, 1983). At more typical environmental baseline levels of 1-10 ng/g this variation could increase to 50-100% (Holden *et al.*, 1983). By analogy changes in bias over extended time periods may be the major source of the increase in within-laboratory long term variation.

These sources of error can be significantly reduced by good working practice, although this is, in itself not sufficient. For an analytical method to be truly under control, the precision and bias of the method must be continuously assessed by an ongoing quality control programme which will detect any deviation from agreed performance criteria and allow corrective action to be taken (eg Wells and Kelly, in press). Given such control, a long term precision of 10-30% is achievable for baseline organic analysis and is essential if the analysis is to be used in monitoring changes in the environment.

3.2 Field Variance

The results for the analysis of the sediments are listed in Table 2. The effect of depth and core on contaminant levels was examined using ANOVA (Table 3). This examination tested whether a depth related contaminant profile existed in the sediment, thereby indicating the degree of vertical mixing present since a site with a homogeneous vertical profile would not be suitable for trend monitoring. The study was also designed to establish whether there were significant differences between cores. If the cores were not significantly different then the sediment population variance can be obtained from an ANOVA residual sums of squares. If they are significantly different the sediment population variation can be estimated from the between-cores sum of squares.

The multiple analyses of a single sample used for assessment of the short term analytical variance were replaced by a single value equal to their mean. An F-test at p=0.05 showed a significant between-depths difference exists for CBs 101, 118, 153, 138 and 180 and for HCB, lindane and 4,4′-DDE. Between core differences were observed for 4,4′-DDE and 4,4′-DDT. Examination of the data (Table 2) suggests that these are due to single values which are particularly high or low rather than to any core effect. Therefore, there appears to be no between-core variation.

The effect of normalisation of the data using the sediment total organic carbon content (TOC), was investigated for CB118 and CB28 (Table 4). For CB118 the significance level for between core difference decreases from p=0.77% for unnormalised data, to p=0.068% for organic carbon normalised data. In the case of CB28, normalisation produces a significant between depth effect (p=0.002%), and also decreases the significance level of the between core effect. Normalisation using TOC actually increases the difference both between depths and between cores. A physical explanation for this may be non-equilibrium behaviour of sediment bound organochlorine contaminants at this site. Organic carbon is not conservative and decreases with depth (Table 2), whilst more refractory organochlorine contaminants remain at concentrations determined primarily by the historical input and not related to existing sediment organic carbon levels.

In the more usual case, where the sediment being monitored has a low TOC content, normalisation on this basis may be expected to reduce and not increase variance. Only where the unique features of high input rate, high TOC and removal of organic carbon exist is such normalisation inappropriate.

The untransformed data has, therefore, been used for the statistical analysis since the variance is lower for the raw data which has not been normalised to the sediment TOC. Given that no between-core effect has been observed in these data, a one-way ANOVA by depth was used to estimate the residual variance. The residual variability derived from the ANOVA is the sum of the "field" and "short term analytical" variance components and by subtracting the latter, which is known, a value for the "field" variance may be determined (Table 5). The field variance is generally less than 30%, with the exception of CB28 at 65% and 4,4'-DDT at 48%. These data may be averaged to obtain an estimate of the true coefficient of variance associated with field error, ie CV(f) = 25.5% ± 1.04, p=0.005, n=12.

4. STRATEGY

The sensitivity of a technique to detect a change in mean contaminant level on two different sampling occasions is dependent on the confidence interval of the sample means at each occasion. A simple statistical test to assess whether a decrease has occurred in the mean contaminant level is a one-sided "t" test (Box *et al.*, 1978). Suppose that n measurements are made on each sampling occasion. Let $\bar{x}_1$, $\bar{x}_2$ be the corresponding sample means and let S^2 be an estimate of the residual variance. Then the null hypothesis that the true mean of the population has not decreased is rejected if the t statistic

$$t = \frac{\bar{x}_1 - \bar{x}_2}{S\left(\frac{1}{n} + \frac{1}{n}\right)^{\frac{1}{2}}} = \frac{\bar{x}_1 - \bar{x}_2}{S\sqrt{\frac{2}{n}}}$$

is greater than $t_{\alpha,2n-2}$, the appropriate percentile of a t-distribution on 2n-2 degrees of freedom.

Therefore, for the null hypothesis to be rejected:

$$\frac{\bar{x}_1 - \bar{x}_2}{S\left(\frac{2}{n}\right)^{0.5}} > t_{\alpha,2n-2}$$

$$\Rightarrow \quad \bar{x}_1 - \bar{x}_2 > t_{\alpha,2n-2} \cdot S\left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{0.5}$$

Assuming $\bar{x}_1 > 0$, this can be represented in terms of percentages as:

$$\Rightarrow \quad \frac{100.\ (\bar{x}_1 - \bar{x}_2)}{\bar{x}_1} > t_{\alpha,2n-2} \cdot \frac{S\left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{0.5} \cdot (100)}{\bar{x}_1}$$

observed % difference > $t_{\alpha,2n-2}$ CV

The term $t_{\alpha, 2n-2}$. CV can be considered as the critical value for the test and will be termed "Cm". If the observed percentage difference in the mean is greater than Cm it can be concluded that the underlying mean contaminant level has decreased. Given that a specified decrease in the underlying mean contaminant levels has occurred, then as the critical value gets smaller, that decrease will be more likely to be detected. This is because Cm is related to the precision of the difference between the two sample means. "Cm" can thus form the empirical basis for exploring the effect of differing sampling and analytical schemes on the ability to detect changes in contaminant levels. Cm can also be regarded as an approximate indicator of the real level of change in contaminant levels which can be detected.

One major factor in determining the magnitude of "Cm" is the "t" term. The value of "$t_{\alpha,2n-2}$" is governed by the number of independent measurements on the population. Independent measurements may be either individual samples individually analysed, or pools of samples. As the number of degrees of freedom applicable to the comparison of two means of "n" measurements is equal to 2n-2, it is apparent that the extreme of bulking all samples into one large pool will not permit calculation of a critical value to test the sample means. The variance of the mean of a set of pooled samples can be expressed as:

$$\text{Var(mean)} = \sigma_a^2 /PA + \sigma_f^2 /PM$$

P = number of pools
M = samples per pool
A = analyses per pool
σ^2_a = long term analytical variance
σ^2_f = field variance

In terms of this relationship, the critical value "Cm" can be expressed as below with 2P-2 degrees of freedom.

$$Cm = 100.t_{\alpha, 2p-2} \quad (2\sigma_a^2/PA + 2\sigma_f^2/PM)^{0.5}/\bar{x}_1$$

It is preferable to maintain the same pool size for subsequent monitoring at a chosen site, as this simplifies statistical analysis and can avoid bias in the estimation of the mean (ICES, 1990b).

If one analysis is performed per pool, the critical value "Cm" at a probability level of p=0.05 produced by varying numbers of sample pools and samples per pool is illustrated in Figure 2 for CB118. This chlorobiphenyl is typical of the majority of compounds examined with the field variance (CV = 32.4%) and long-term analytical variance (CV = 22%) of comparable magnitude and close to the average values for the chlorobiphenyls. A rapid decrease in "Cm" occurs as the number of pools and the corresponding number of degrees of freedom increase. The effect is greatest for small numbers of pools with "t" decreasing from 2.92 with P=2 to 1.73 with P=10. Higher numbers of pools result in little further decrease. Figure 2 demonstrates that "Cm" is relatively insensitive to the number of samples per pool. The major determinand is the number of pools.

The effect of increasing the number of analyses per pool is illustrated in Figure 3. An increase from one to two analyses per pool results in a decrease in Cm of around 12% with little further decrease achievable for greater numbers of analyses. As any increase in this parameter means a substantial increase in both commitment of analytical resources and expenditure, greater precision is not easily achieved by this route.

The relative importance of analytical and field variances in determining the magnitude of the critical value "Cm" is illustrated in Figure 4. For both chlorobiphenyls CB28 and CB153, values for long term and short term analytical variances have been used to calculate the confidence interval "Cm" for varying numbers of pools. Only a minor decrease in the width of the confidence interval for both congeners results from using the smaller short term variance. For P=10 Cm [CB28] declines from 38.8% to 36%, whilst Cm [CB153] declines from 19.8% to 12.2%. The magnitude of this decrease is similar although the ratio of long term to short term analytical standard deviation is 3 for CB28 and 1.3 for CB153. The overall variance of CB28 is dominated by the field variance. This exemplifies the dominance of the inherently large sampling and population variance in determining the precision of any estimate of environmental contaminant concentrations. The contribution of the analytical error associated with an analytical procedure which is under control to the overall precision of a measured value will be small.

When the measured variances are applied to the Garroch Head sediment samples then it is possible to achieve a level of precision, as expressed by the critical value "Cm", of around 25% without undue cost or effort. In terms of analyses this would require either 14 analyses of individual samples, 10 analyses of 20 samples or seven analyses of 28 samples.

A common sampling scheme used at this and other laboratories has been to take five replicate samples at a site and singly analyse. Applying these variance values to the analysis of the five samples would give a critical value for the t-test for repeated sampling of Cm = 46%. In areas with high natural sediment accretion of up to 1 cm per year such as the inner German Bight and the Skaggerak/Norwegian Channel (Eisma and Kalf, 1987), the use of such a sampling scheme may detect at best a 50% decrease in input, after one year, provided that this decline was also mirrored as a decrease in sediment concentration. In offshore areas where accretion rates are less than 0.1 cm per year, a longer interval would be required to detect a similar decrease in input, though in practice sediment mixing processes could substantially increase these estimates.

5. ECONOMIC ANALYSIS

Once the analytical and field variance has been determined the sampling cost relative to a desired level of precision can be estimated. The total cost (C) is calculated from number of analyses (PA), costing (C_n) each and number of samples (PM), costing (C_h) each, ie:

$$C = C_n.PA + C_h.PM$$

Any combination of P, M and A to achieve a given precision can be readily obtained using spreadsheet calculations. The cost of each monitoring strategy can then be evaluated by application of these parameters to the cost equation. The cost of sampling and analysis will depend on the vessel used and the consumable and capital costs of the analytical

laboratory. For example the sampling cost could be estimated at £100 per sample, based on a small sea-going ship costing £2,500 per day, with 25 samples taken per day. Analytical cost could be estimated at £240 per analysis, which includes staff, consumables, overheads and depreciation of all equipment over a five year period. This is based on one analyst for six days processing a batch of nine samples with appropriate quality control samples and 10% duplicate samples. In this type of routine analysis, ~40 determinands would generally be quantified. On this basis, a cost of £6 per determinand would be associated with the analytical process.

The most economic sampling scheme and associated costs applied to monitoring of CB118 in Garroch Head sediment is listed in Table 6. As the critical value "Cm", increases, the costs escalate exponentially as illustrated in Figure 5. A high degree of precision can only be achieved by considerable investment of both time and money. Table 6 demonstrates that the most cost effective policy is:

- to analyse pooled rather than individual samples
- to analyse a number of pools containing a small number of individual samples
- only undertake one or two analyses per pool

The analysis of individual samples would give the most precise estimate of the mean, but this is also the most costly. By pooling samples the same number of individuals can be analysed, but at a much lower cost, and with only a small decrease in precision. This is most true when target precision is high. The most economic approach to achieving a precision of Cm <25% for CB118 in Garroch Head sediment is to analyse samples in pools of two or more.

As a further example, assume that the site to be monitored is more uniform than Garroch Head and the field variance associated with sediment contaminant measurements is less at 20%. The levels of organochlorine contaminants at such a "clean" site would typically be 1-10 ng/g. As a contrast to the calculations for the Garroch Head site the analytical variance could be increased in line with the Horowitz relationship (Horowitz *et al.*, 1980), from the 20-30% observed for Garroch Head sediment to ~40%, however in practice a laboratory whose analytical method is under control is unlikely to increase analytical variance at these lower contaminant levels.

Using these figures, with a sampling cost of £100 and an analytical cost of £240, the most economic sampling schemes for various values of Cm can be calculated (Table 7). In this example, higher analytical variance has favoured duplicate analyses of sample pools. The reduced field variance as compared to Garroch Head has required fewer samples to be taken.

CONCLUSIONS

This empirical study has served to illustate that the predominant contribution to the variance of estimated mean concentration of organochlorine contaminants in sediment derives from the sampling procedure and the variance of the sediment population itself, termed the "field" variance. The contribution of the variance associated with the appropriate analytical procedure, which is under under control, is small. Having achieved a long term analytical variance of 20-30% or less further improvements will have little influence on the precision of environmental measurements. Those who design environmental monitoring programmes must recognise the limitations imposed by natural "field" variance on the ability to measure spatial and temporal trends in the environment. Any programme with this stated aim must focus on a sampling and analytical scheme which will minimise such variance. This requires knowledge of both the long term analytical variance, evaluated through regular analysis of a Laboratory Reference Material, and the field variance, which can be estimated for the site to be monitored through a pilot study. Field variance may range from 20-50% depending on the location and properties of the site.

The precision of an estimate of a mean contaminant level in the sediment relies primarily on the number of replicates taken at that site. The number of replicates required is dictated by both the field variance and the required precision of the mean. Generally, the most cost effective approach is not to analyse individual samples, but to create a number of pools with small sample numbers. An increase in precision is best obtained by increasing the number of pools and not replicate analysis of pools. Pooling of samples does require the distributional properties of the population to be assessed.

In practice, the ability to detect changes in input levels through monitoring of sediment contaminant concentrations will be dependent on the local depositional environment, especially the rates of sediment accretion and sediment mixing. Only areas with moderate to high deposition rates and little sediment mixing will be suitable.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the assistance of Eileen Shanks of the statistics group of the Marine Laboratory, for valuable discussion and assistance in the production of this paper.

REFERENCES

Baxter, M.S., Stenhouse, M.J. and Drndarski, N. 1980. Fossil carbon in coastal sediments. *Nature*, **287**: 35-36.

Box, G.E., Hunter, W.G. and Hunter, J.S. 1978. Statistics for experimenters. John Wiley and Sons, New York.

Cantillo, A.Y. 1989. NOAA Technical Memorandum NOS OMA 51. Standards and reference materials for marine science. Rockville, Maryland, USA.

Craib, J.S. 1965. A sampler for taking short undisturbed marine cores. *J. du Conseil Permanent Int. pour l'exploration de la Mer*, **30**: 34-39.

Eisma, D. and Kalf, J. 1987. Dispersal, concentration and deposition of suspended matter in the North Sea. *J. Geol. Soc.*, London 144, pp161-178.

Holden, A.V., Topping, G. and Uthe, J.F. 1983. Use and Relevance of Analytical Intercomparison Exercises in Monitoring the Marine Environment." *Can. J. Fish. Aquat. Sci.*, **40**: 100-110.

Horowitz, W., Kamps, L.R. and Boyer, K.W. 1980. Quality assurance in the analysis of foods for trace constituents. *J. Off. Anal. Chem.*, **63**: 1344-1354.

Howells, S.E., Dodd, N.M. and Turner, C. 1989. Determination of hydrocarbons in environmental samples: sampling and analytical variability. In: *Ecological Impacts of the Oil Industry* (Dicks, B., ed.) pp135-167.

ICES. 1984. Six-year review of ICES Coordinated Monitoring Programmes. *ICES Coop. Res. Rep.*, No. 126, pp77-100.

ICES. 1987. Report of the ICES Advisory Committee on Marine Pollution, 1986. *ICES Coop. Res. Rep.*, No. 142, pp72-75.

ICES. 1989a. Statistical Analysis of the ICES Cooperative Monitoring Programme data on contaminants in fish muscle tissue (1978-1985) for determination of temporal trends. *ICES Coop. Res. Rep.*, No. 162.

ICES. 1989b. Report of the Advisory Committee on Marine Pollution, 1989. *ICES Coop. Res. Rep.*, No. 167 pp68-76.

ICES. 1990a. Report of the Working Group on Statistical Aspects of Trend Monitoring, 1990, Annex 7.

ICES. 1990b. Pooling may economise a sampling programme, Annex 5. Report of the ICES Advisory Committee on Marine Pollution 1990. *ICES Coop. Res. Rep.*, No. 172.

Krumgalz, B.S., Fainshtein, G., Sahler, M. and Gorfunkel, L. 1989. "Field error" related to marine sediment contamination studies. *Mar. Poll. Bull.*, **20**: 64-69.

Larsen, B. and Jensen, A. 1989. Evaluation of the sensitivity of sediment monitoring stations in pollution monitoring. *Mar. Poll. Bull.*, **20**: 556-560.

Lohse J. 1988. Distribution of organochlorine pollutants in North Sea sediments. In: *Biogeochemistry and Distribution of Suspended Matter in the North Sea and Implications to Fisheries Biology* (Kempe, J. *et al.*, eds) Mitt. Geol.-Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderbd. **65**: 345-365.

MacKay, D.W. 1986. Sludge dumping in the Firth of Clyde - a containment site. *Mar. Poll. Bull.*, **17**: 91-95.

NSTF. 1990. North Sea Task Force Report, No 3. Monitoring Master Plan, London.

OSPARCOM. 1990. Monitoring Manual of the Oslo and Paris Commissions, OSPARCOM 9/11/1, Annex 5.

Pheiffer Madson, P. and Larsen, B. 1986. Accumulation of mud sediments and trace metals in the Kattegat and the Belt Sea. Report of the Marine Pollution Laboratory No. 10.

Uthe, J.F. and Musial, C.J. 1980. Report on the 5th ICES intercalibration study of PCBs in biological material. *ICES Coop. Res. Rep.*, No. 115.

Wells, D.E. 1988. The need for organic reference materials in marine science. *Fresenius Z. Anal. Chem.*, **332**: 583-590.

Wells, D.E., Cowan, A.A. and Christie, A.E.G. 1985. Separation of organochlorine residues by adsorption chromatography prior to capillary gas chromatography. *J. Chrom.*, **20**: 556-560.

Wells, D.E. and Kelly, A.G. In press. Progress in the quality assurance of trace organic analysis. *Microchim. Acta.*

TABLE 1

Analytical variance for organic trace contaminants in Garroch Head sediment and laboratory reference material LRM 125

Determinand	Short term analytical variance			Long term analytical variance		
	n	Mean	CV%	n	Mean	CV%
CB28	4	17.1	7	10	34.1	20
CB52	4	59.1	10	10	65.2	24
CB101	4	20.7	8	10	38.1	19
CB118	4	12.3	12	10	32.1	22
CB153	4	29.3	16	10	43.3	20
CB138	4	19.1	9	10	51.0	21
CB180	4	21.6	11	10	44.9	21
HCB	4	4.3	28	10	2.8	39
γ-HCH	4	10.3	18	10	8.2	29
4,4′-DDT	4	11.6	8	10	86.0	79
4,4′-DDE	4	11.8	8	10	11.6	40
4,4′-DDD	4	37.1	10	10	58.1	25

TABLE 2

Sediment concentration (ng/g dry wt)

	Position	TOC %	CB28	CB52	CB101	CB118	CB153	CB138	CB180	HCB	G-HCH	4,4′-DDD	4,4′-DDT	4,4′-DDE
1	55°39.88′N	11.99	9.30	50.59	17.21	9.99	30.81	13.95	19.09	6.66	11.46	21.58	9.39	25.00
2	5°00.79′W	9.30	28.59	77.31	20.33	14.30	33.73	17.84	19.64	5.07	3.65	19.07	6.50	26.56
3		8.68	28.32	67.60	30.05	21.93	40.32	27.55	28.59	5.76	31.60	25.62	8.04	38.44
4		3.34	15.75	25.82	13.39	9.23	17.28	11.45	12.84	0.87	1.74	18.11	7.18	20.08
1	55°39.91′N	9.48	15.75		22.07	10.69	33.66	15.27	22.56	4.30	12.15	24.53	109.57	133.31
2	5°00.99′W	9.87	13.95	55.73	23.67	14.57	34.42	18.04	22.56		4.23	22.11	11.61	11.61
3		8.55	53.02	98.76	44.49	33.52	60.24	42.06	49.27	4.59	4.86	36.36	16.57	62.44
4		3.24	32.13	37.20	21.72	13.46	29.01	20.47	23.25	1.27	3.61	13.58	11.03	34.28
1	55°39.95′N	10.58	16.03	118.47	22.07	10.69	33.66	15.27	22.56	6.84	9.14	40.80	18.21	38.27
2	5°01.20′W	10.48	37.82	68.01	25.54	18.74	34.42	23.46	21.17	9.23	4.69	26.92	14.45	43.25
3		9.52	58.09		30.47	20.61	42.33	25.33	29.77	5.62	5.62	20.28	6.69	37.95
4														
1	55°39.83′N	9.60	34.56	98.27	26.51	16.03	34.63	21.86	22.62	3.98	4.90	25.70	6.13	30.63
2	5°00.80′W	6.64	29.08	63.50	24.50	16.10	27.76	19.22	19.43	4.65	5.59	15.61	2.17	30.76
3		4.55	29.84	40.46	32.06	20.47	39.49	27.62	30.12	1.46	3.37	15.51	3.30	42.16
1/1	55°39.87′N	9.63	11.38	40.81	17.14	9.30	23.67	15.82	19.78	2.84	5.42	22.44	7.03	21.68
1/2	5°00.69′W		15.62	56.84	22.42	14.44	30.67	21.51	21.79	4.75	8.90	29.02	8.27	26.80
1/3			17.49	61.56	20.40	12.08	33.03	18.32	21.03	5.66	7.31	24.82	7.30	27.49
1/4			18.53	65.44	18.46	11.03	22.62	17.84	18.81	2.89	6.26	22.85	7.93	24.28
1/5			16.66	52.33	21.44	11.80	30.81	18.67	24.71	3.81	6.06	26.34	8.57	27.86
2		9.24	33.45	73.22	35.95	21.10	42.89	27.14	31.92	6.19	3.29	24.18	3.73	40.24
3		5.53	20.40	25.89	25.05	17.23	35.53	22.00	26.72	0.62	3.16	16.66	5.17	30.36

TABLE 3

Two-way ANOVA by core and depth of organic contaminants in Garroch Head sediment

Determinand	Between cores		Between Depths		Residual
	n	Significance (p=0.05)	n	Significance (p=0.05)	n
CB28	4		3		9
CB52	4		3		7
CB101	4		3	*	9
CB118	4		3	*	9
CB153	4		3	*	9
CB138	4		3	*	9
CB180	4		3	*	9
HCB	4		3	*	8
γ-HCH	4		3	*	8
4,4'-DDT	4	*	3		8
4,4'-DDE	4	*	3	*	9
4,4'-DDD	4		3		9

TABLE 4

ANOVA by depth and core of sediment data for CB118 and CB28. Data has been normalised to the sediment percentage organic carbon content

		CB118				CB28			
		unnormalised		normalised		unnormalised		normalised	
	df	F	p	F	p	F	p	F	p
Depth	3	5.75	0.018	19.06	0.000	2.12	0.168	11.21	0.002
Core	4	0.46	0.776	3.20	0.068	0.91	0.499	2.37	0.130

TABLE 5

Field variance for Garroch Head from analysis of variance components

Determinand	n	Residual error	Short term analytical variance σ^2_A	Field variance σ^2_F	Field CV%
CB28	13	147.3	1.5	145.7	65.1
CB52	11	626.8	32.4	594.3	35.1
CB101	13	32.9	2.9	30.0	25.2
CB118	13	17.1	2.2	15.0	32.4
CB153	13	44.4	20.9	23.5	14.9
CB138	13	29.7	2.8	27.0	30.3
CB180	13	39.4	5.9	33.5	26.8
HCB	12	3.5	1.4	2.1	26.0
γ-HCH	12	7.4	3.5	3.9	15.3
4,4'-DDT	12	53.1	0.6	52.5	48.2
4,4'-DDE	13	14.4	1.0	13.4	27.4
4,4'-DDD	13	96.4	14.1	82.4	22.7

TABLE 6

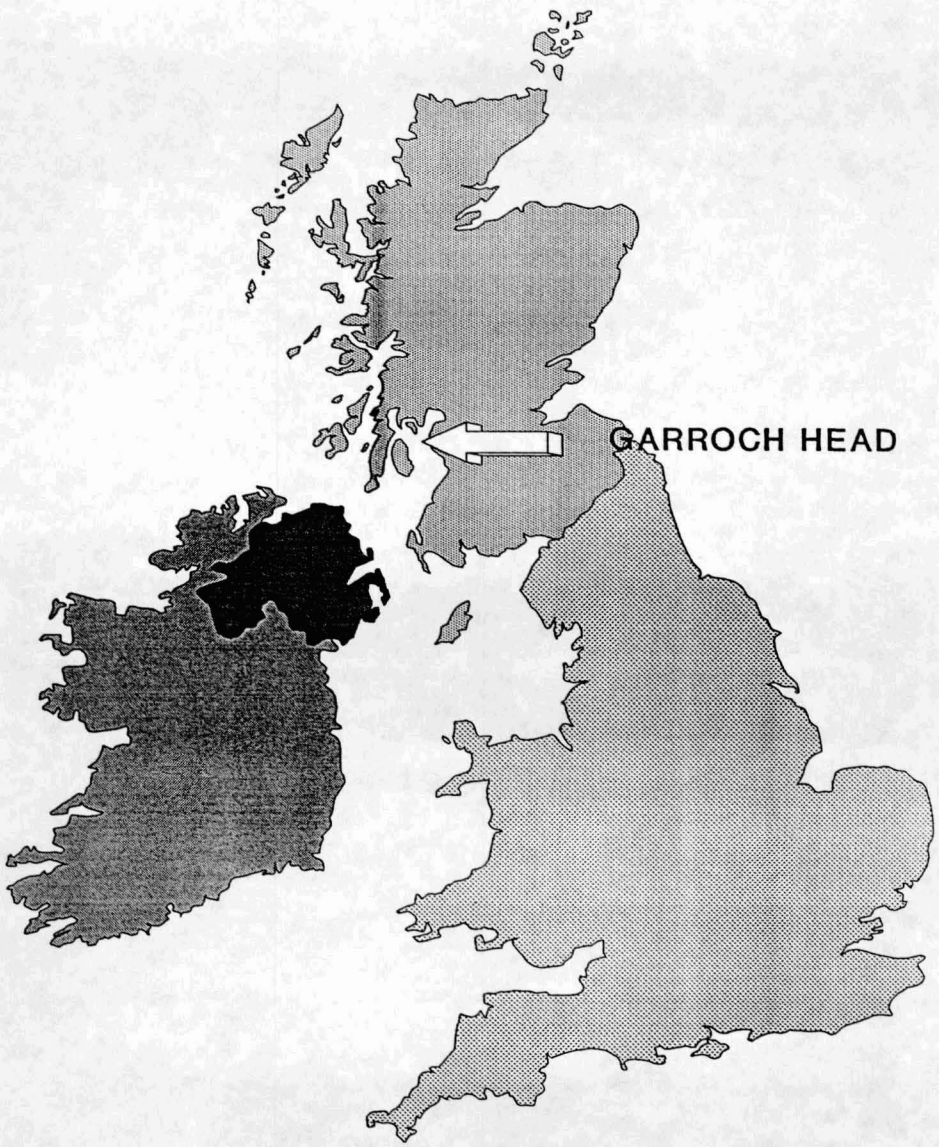
Most economic sampling schemes for organochlorine contaminants at the Garroch Head sludge disposal site to achieve a given critical value "Cm". Data is based on CB118 with field CV = 32.4% and analytical CV = 22%. Sampling cost = £100, analysis cost = £240

Critical value Cm (%)	Pools P	Samples per pool M	Analyses per pool A	Cost (£)
10	18	7	3	25,560
	20	6	3	26,400
	28	4	2	24,640
15	10	5	3	12,200
	15	3	2	11,700
	25	2	1	11,000
20	7	4	3	7,840
	7	5	2	6,860
	8	3	3	8,160
	9	3	2	7,020
	22	1	1	7,480
25	5	4	3	5,600
	5	5	2	4,900
	14	1	1	4,760
30	6	2	2	4,080
	7	2	1	3,080
	10	1	1	3,400
35	4	3	2	3,120
	8	1	1	2,720
40	4	3	1	2,160
	5	2	1	2,200
	6	1	1	2,040
50	4	1	1	1,360
	5	1	1	1,700

TABLE 7

Most economic sampling schemes for organochlorine contaminants in sediment at a "clean" site to achieve a given critical value "Cm". Assumed field CV = 20% and analytical CV = 40%. Sampling cost = £100, analysis cost = £240

Critical value Cm (%)	Pools P	Samples per pool M	Analyses per pool A	Cost (£)
10	18	5	7	39,240
	28	2	5	39,200
15	23	1	3	18,860
	30	1	2	17,400
20	10	3	3	10,200
	17	1	2	9,860
	27	1	1	9,180
25	9	1	3	7,380
	12	1	2	6,960
	19	1	1	6,460
30	7	1	3	5,740
	9	1	2	5,220
	13	1	1	4,420
35	5	1	3	4,100
	7	1	2	4,060
	10	1	1	3,400
40	5	1	2	2,900
	8	1	1	2,720
50	4	1	2	2,320
	5	2	1	2,200
	6	1	1	2,040



LOCATION OF GARROCH HEAD SEWAGE SLUDGE DISPOSAL SITE. FIRTH OF CYLDE

FIGURE 1

CRITICAL VALUE 'Cm' WITH VARYING NUMBERS OF POOLS 'P' AND SAMPLES PER POOL 'M' FOR CB 118 IN SEDIMENT

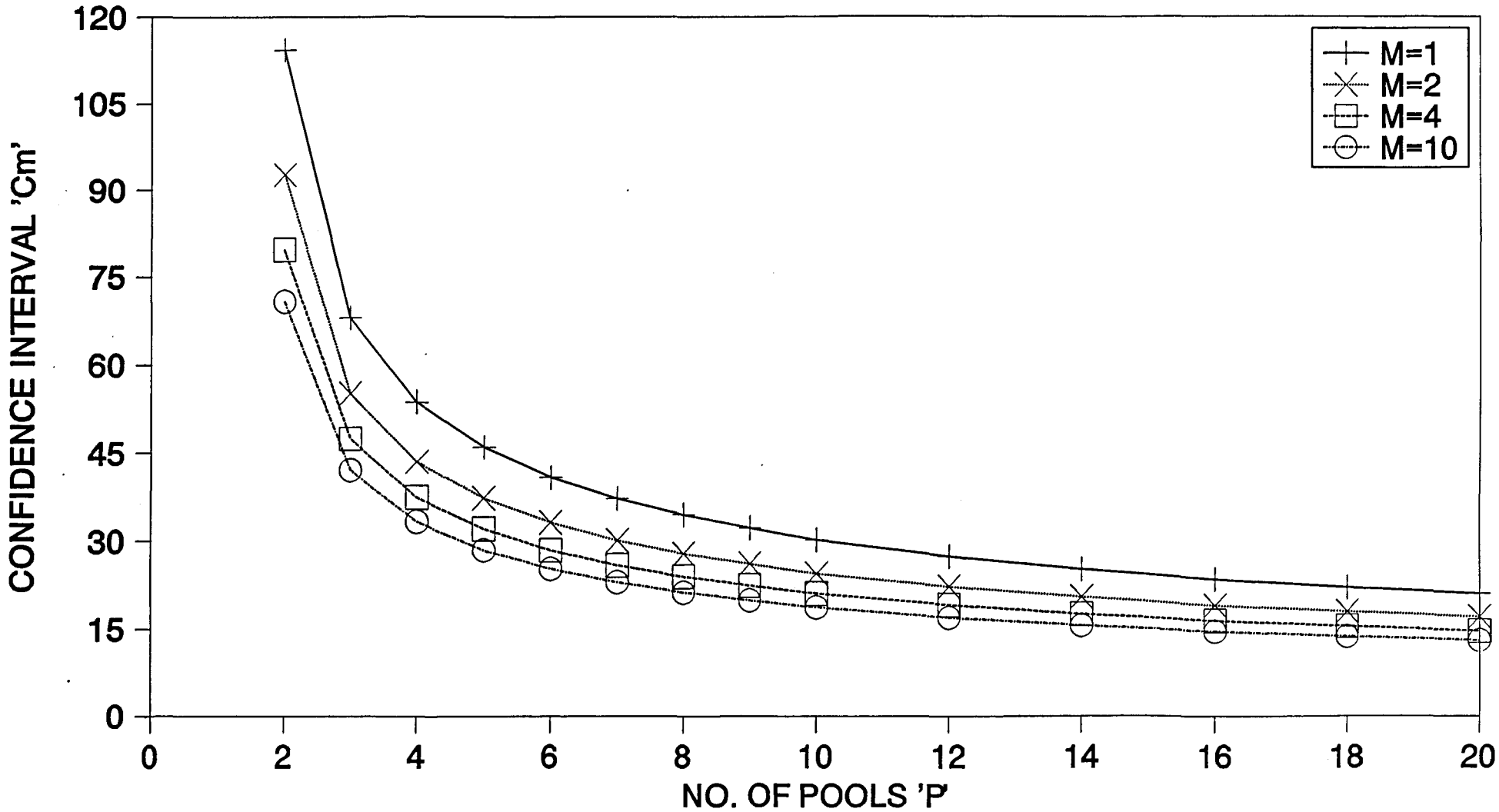


FIGURE 2

EFFECT ON VAYING 'A' AND POOLS 'P' ON CRITICAL VALUE 'Cm' FOR CB118 IN SEDIMENT. SAMPLES PER POOL 'M'=2

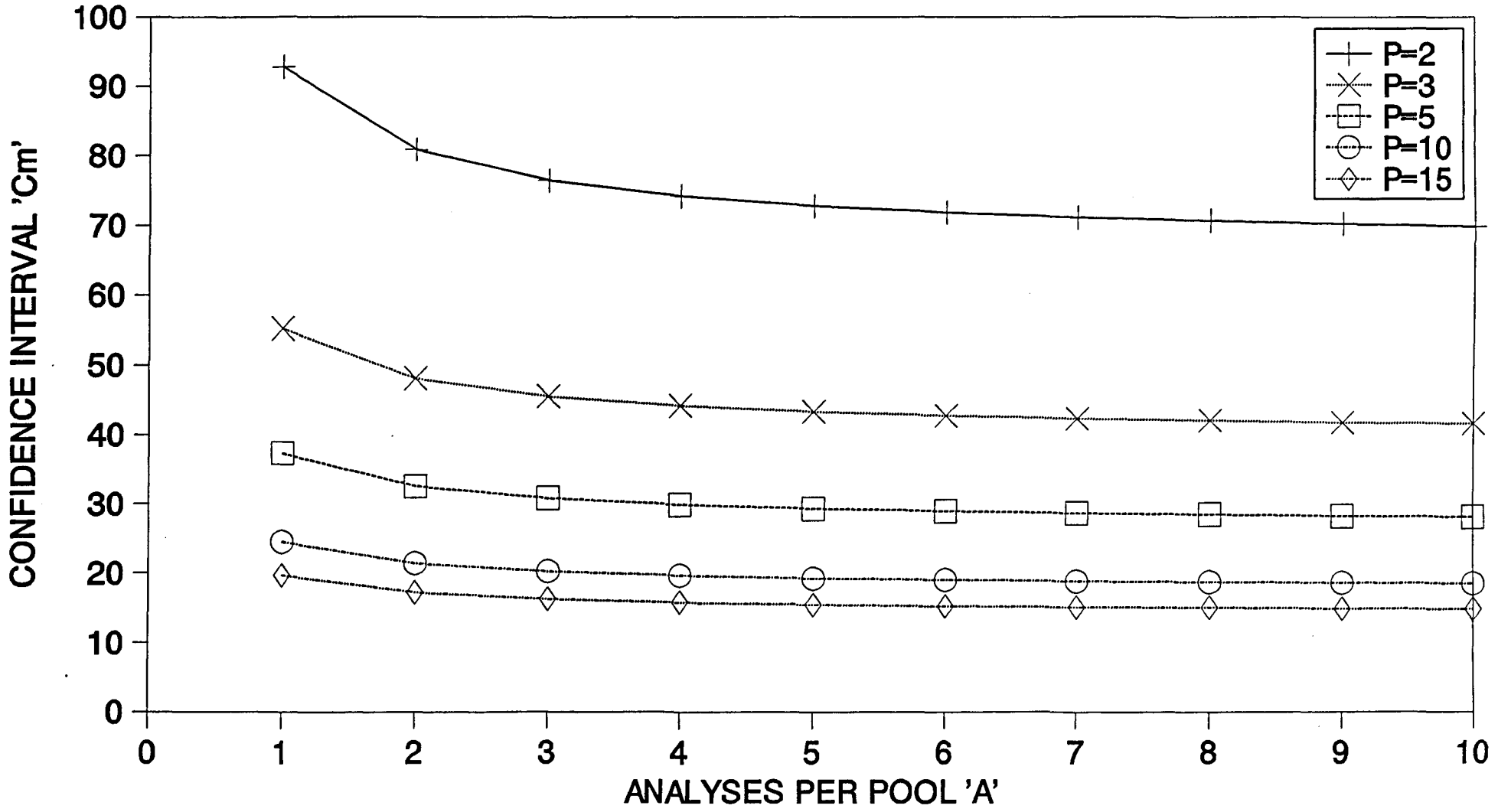


FIGURE 3

COMPARISON OF EFFECT OF LONG-TERM AND SHORT-TERM ANALYTICAL VARIANCE ON 'Cm' FOR CB153 AND CB28

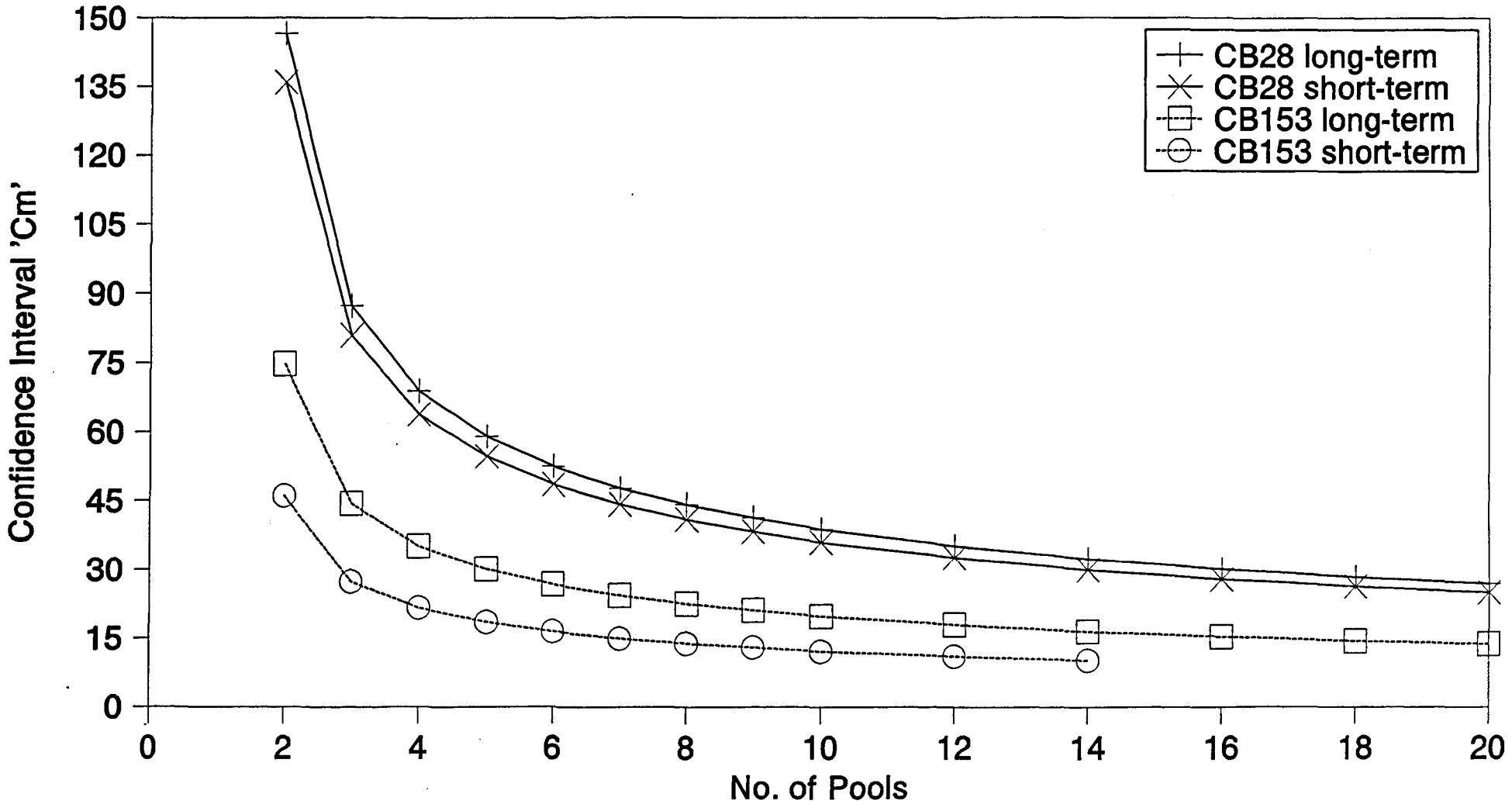


FIGURE 4

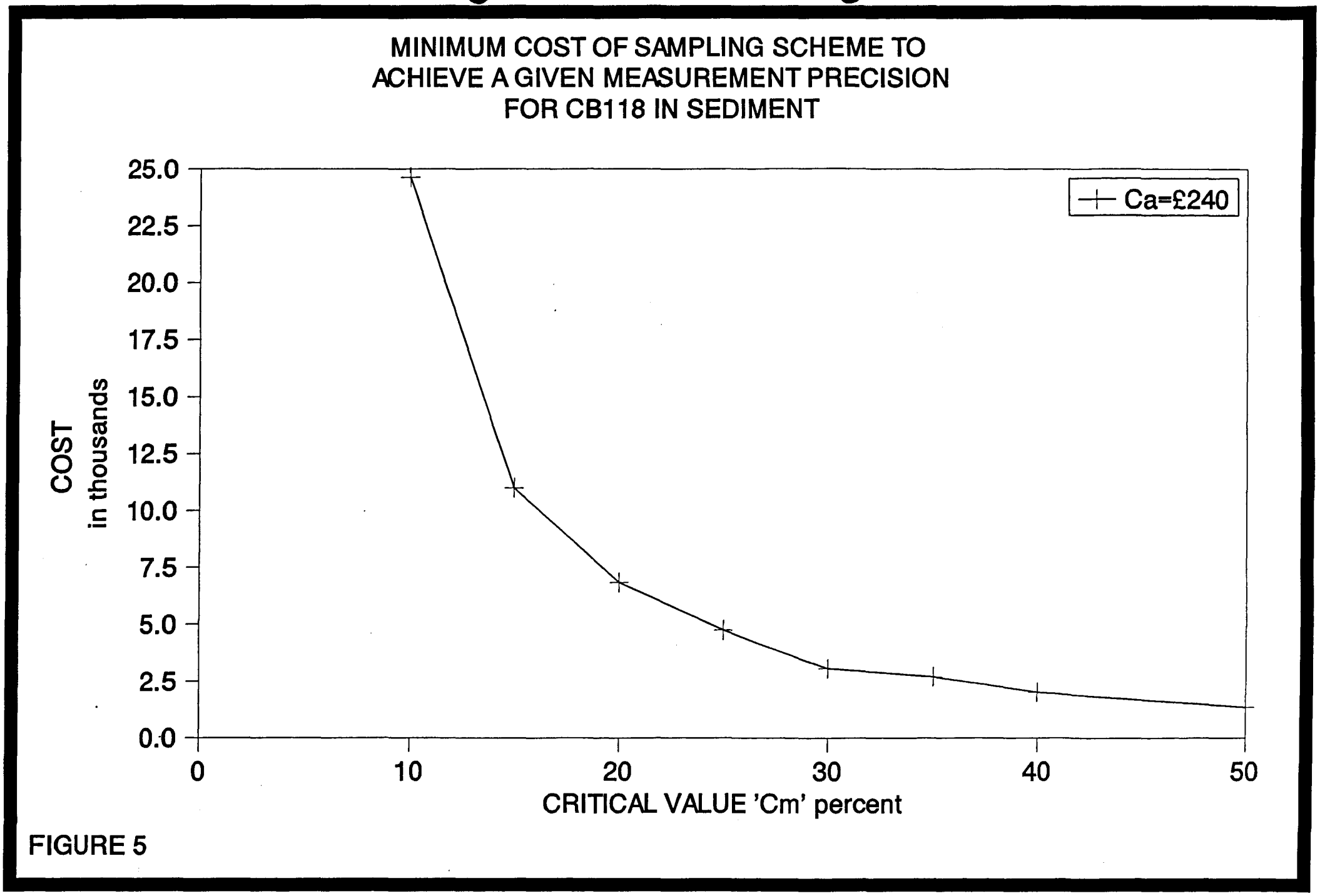

MINIMUM COST OF SAMPLING SCHEME TO
ACHIEVE A GIVEN MEASUREMENT PRECISION
FOR CB118 IN SEDIMENT
COST
in thousands
25.0
22.5
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
0
10
20
30
40
50
CRITICAL VALUE 'Cm' percent
Ca=£240

FIGURE 5