

Sampling Surficial Sediments of a River Receiving Minewater Discharges

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ABSTRACT

Metal contamination of sediments can be an issue for minesites discharging water. Water sampling of receiving waters is frequently undertaken. Sampling and analysis of sediment is less common. The variability of receiving environments makes the formulation of a generic sediment sampling strategy virtually impossible. Each situation needs to be carefully assessed before sampling is undertaken. This paper outlines the approach taken for one such survey.

The main factors that need to be considered in a survey of surficial sediments are sample representativeness and sample variability. A simple data set from one site within a regional survey is used to illustrate the importance of these factors. The metal content of sediment is shown to vary significantly over small spatial scales.

The variability associated with the spatial distribution of samples within a site is shown to be the most significant source of variability in the study. This variability could bias the results of a study if not planned for in the sampling methodology. Taking multiple samples from within each site (sub-site samples) and combining the data gives a more representative indicator of overall conditions than a single sample. The optimum number of sub-site samples to be taken from each sampling site was found to be 15.

It is shown that a composite of sub-site samples can give a good indication of the average site metal content, while considerably reducing the sample preparation and analysis effort.

INTRODUCTION

Clarence Colliery is located about 100 km west of Sydney, near Lithgow. Approximately 14ML of water per day, including underground dewaterings and site drainage, is treated to Environmental Protection Agency (EPA) licence requirements and released into the Wollangambe River. The licensing requirements on the water released are comparably stringent to drinking water standards. A study of the metal concentrations in the sediments of the Wollangambe was initiated as part of the development of Clarence Colliery's environmental best practice program.

Six sites were sampled for the Wollangambe River regional sediment study, along a 25 km stretch of the river. Multiple samples were collected from each of the sites and analysed to determine the concentration of key metals in the surface layer of the sediment. Previous data was used to select the metals to be included in the study. The metals selected were cobalt, iron, manganese, nickel and zinc. The mass of the metals per unit area of the riverbed was calculated for each site. A regional picture of the Wollangambe River was developed from this data.

Multiple samples were collected from spatial locations that varied over a small distance (of the order of metres) at each of the sampling sites. This enabled the variability associated with the spatial location of the sediment metal concentration to be assessed for each of the sites. This variability was then compared to the variability associated with the preparation and analysis of the samples to assess its significance. The optimum number of sub-site samples required to achieve a figure representative enough of the true sediment metal concentration was evaluated.

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STUDY METHODOLOGY

Sampling

The Wollangambe River system is a highly variable environment. The river rapidly changes from sections of fast flowing riffle to slow moving pools. A wide variety of depositional environments are encountered, even over a small area of the order of just a few square metres. Taking a sample from just one of these environments would not provide data indicative of the overall conditions for that site on the river. For the data to have meaning in the development of a regional picture of metal contents many samples must be taken from each site and an average metal content for the site calculated. This reduces the risk of small-scale spatial variability of the sediment metal content biasing the data collected.

A research program was conducted on the sampling of sediment in rivers. Previous work conducted indicates that sediment can exhibit considerable variation at all spatial scales (Morrisey *et al*, 1994). Such variation lead Herr and Gray (1997) to conclude that subsite sampling is essential to obtain reasonably accurate estimates of the metal concentrations of a specific site. For the Wollangambe River regional sediment survey, it was decided that a nominal number of 25 sub-site samples should be collected from each site. Samples were taken from the nodes of a 2m x 2m grid placed over the river bed area. Fig. 1 shows a graphical representation of the sampling grid used at the first site sampled in the study (site W1). The sample data set upon which this paper is based comes from this site.

Samples were taken systematically from every node of the grid. Systematic sampling provides unbiased results, providing the position of the starting node is randomly selected. A random sampling pattern was considered, however the use of such methods is discouraged (NSWEPA, 1995). Random sampling is statistically unbiased, but the chance of sampling points clustering together makes the method unsuitable for providing an overall picture of the spatial distribution of metals within the sediments of a site.

The surface layer of sediment is subject to the most recent accumulation of metal ions. It is in direct interaction with the water column and river biota (Herr and Gray, 1997). The top 25 mm of sediment was sampled from the river bed and all available material was collected when the depth of the sediment layer was under 25 mm.

Sediment samples were collected using a PVC plastic cylinder of 100mm diameter and 25 mm depth. One end of the cylinder was open to allow it to be driven into the sediment. A hole was drilled in the enclosed end of the cylinder to enable water to escape as the cylinder was driven into the sediment. After the cylinder was driven into the sediment, a stiff piece of plastic was inserted under the open end of the cylinder. The cylinder containing the undisturbed sediment sample was then withdrawn and the sample placed in labelled zip-lock plastic bags. The bag was then placed in another bag to ensure security of the sample during transport.

For the purposes of the Wollangambe regional sampling program, biofilms were considered an integral part of the river's sedimentary system. Layers of biofilm were thus sampled for inclusion in the study when encountered. Biofilms are defined as an assemblage of immobilised microbial cells (mainly bacteria) bound into a matrix of excreted extracellular polysaccharides (Ragusa, 1996). Biofilms generally form at the solid/water interface due to the fact that nutrients often concentrate where surface charges exist on solid surfaces. The tangled mats of cells that form can catch and hold sediments as well as adsorb and fix dissolved metals. Biofilms were collected and subsequently analysed using the same techniques employed for other collected sedimentary materials.

Samples of biofilm were collected by placing an open ended PVC cylinder over the surface to be sampled and loosening the biofilm within the cylinder with a plastic scraper. The biofilm was then collected with a plastic suction pump. The cylinder used was of the same area dimensions as the one used to collect sediment samples.

Many sections of the river were flowing rapidly, which made collection of samples difficult. The sampling equipment used was developed primarily in response to the need to collect samples in a way that minimised the loss of the sample in the flowing water. The samples were visually classified, based on grain size, at the time of collection. The categories for the sediment material collected were sand, fine sand, mud and biofilm.

Analysis

The mass of sediment for the area sampled at each node was determined in the lab by drying (at 105°C) and weighing. The samples were then homogenised and the sample size reduced using the coning and quartering technique. US EPA Method 3050B (US EPA, 1980) was employed for the digestion of the sediment samples prior to analysis. This digestion technique is a strong acid digest. The metals that are in insoluble particulate form or adsorbed to the surface of the sediment matrix are dissolved into the solution to be analysed. The actual matrix of the sediment material is not broken down.

The digested solutions were then analysed utilising flame atomic absorption spectrometry (APHA, 1995). The accuracy of the analytical result is reflected by how well it agrees with the true quantity of constituent. This was assessed with Standard Reference Materials (SRM's). The SRM used in the Wollangambe River regional sediment study was AGAL 10, a lake sediment sample provided by the Australian Government Analytical Laboratories.

Data Assessment

Assessment of the variability associated with the preparation and analysis of the samples

The precision of a result is reflected by its reproducibility. Replication of analysis was used to give a statistical estimation of the precision of the preparation and analysis techniques employed. Variability data from measurements of replicates from different samples may be combined (or pooled) to give a better estimate of variance, while minimising the number of replicate analysis that are carried out on each sample. It should be noted that this method of pooling is only applicable when the estimates of variability are from the same population. This was the case, as we were estimating the variance of a set preparation method and a single analysis instrument. Variance is often expressed in terms of standard deviation (s). The general equation used to pool estimates of variability from replicates of different samples is shown below:

$$s_a^2 = \frac{(s_1^2 \times df_1) + (s_2^2 \times df_2) + (s_3^2 \times df_3) + \dots + (s_j^2 \times df_j)}{df_1 + df_2 + df_3 + \dots + df_j}$$

where

- s_a = the standard deviation of the preparation and analysis method
- s_j = the standard deviation of the set of replicates
- df_j = the degrees of freedom in the replicate set
- j = the number of subsite samples

In the analysis of sub-site samples from the trial site, it was decided that two replicate samples would be made from each sub-site sample. These duplicates were analysed and the standard deviation estimated from the two values obtained. This represents an estimation of variance made with one degree of freedom ($df=1$), as two samples were used to calculate the standard deviation.

Assessment of Small Scale Variability

The variability associated with the preparation and analysis of the samples (represented by the standard deviation s_a) was used to estimate the variability associated with the spatial distribution of the sub-site samples (represented by the standard deviation s_s). Mean values were calculated for each sub-site sample based on the duplicate analyses. The standard deviation of the sub-site samples was calculated using the mean values of the metal concentrations for each set of sub-site replicates. Fig. 2 represents the nested structure of the sampling and analysis for the site.

Values s_s for level 2 were calculated from the mean of level 3 values. The pooled variance from level 3 was calculated to give an estimate of the variance associated with analysis of the sub-site samples (s_a). The value for level 1 was calculated from the mean of the level 2 values. The variance from level 2 was calculated and used to estimate the variance associated with the spatial distribution of the sub-site samples (s_s).

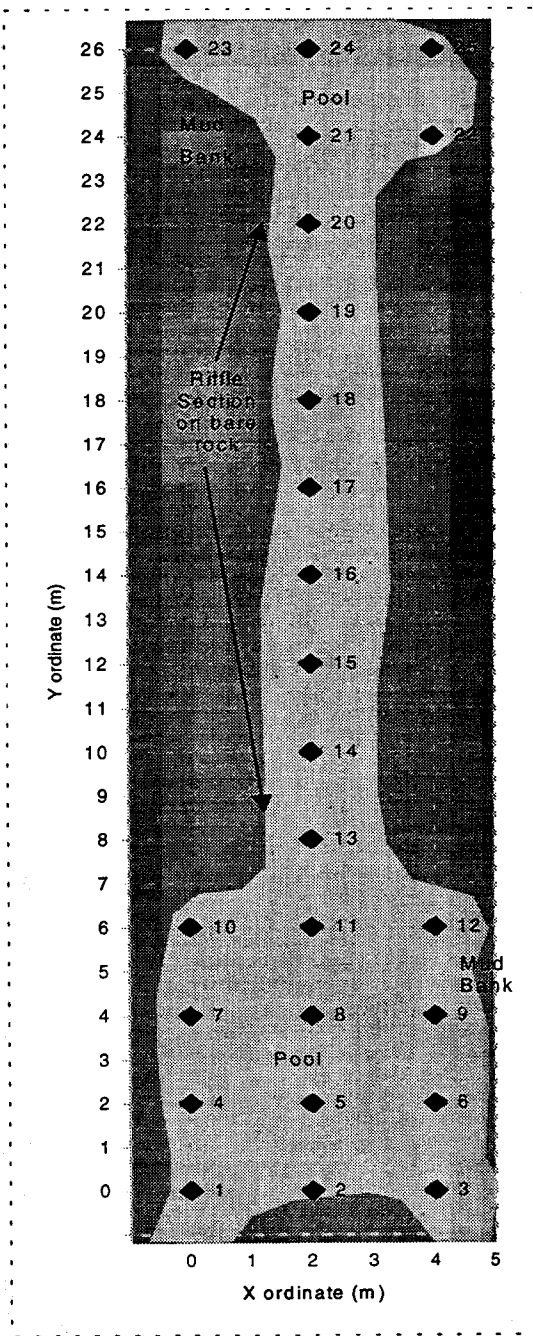


Fig. 1 - Sampling grid pattern used at the first site sampled in the study

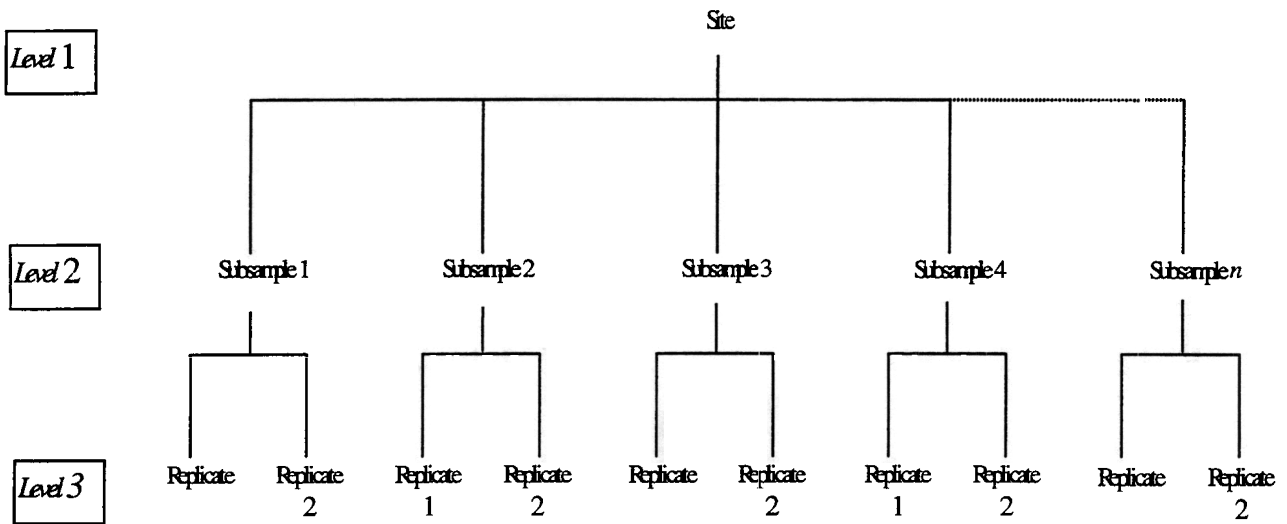


Fig. 2 - Nested design for analysis of variance of trial sampling sites

The variability associated with the spatial distribution of the sub-site samples within the site was calculated as follows:

$$s_s = \sqrt{s_{sample}^2 + \frac{s_a^2}{2}}$$

where

- s_s = the standard deviation of the spatial distribution of the samples
- s_a = the standard deviation of the preparation and analysis method
- s_{sample} = the standard deviation of the sample values

The relative sizes of the sources of variability for the overall site and within each sediment category for iron are shown for iron in Fig. 3. The variability associated with the preparation and analysis of the samples is generally much smaller than the variability due to the spatial distribution of the sub-site samples. The exception was the fine sand samples where the variability associated with the preparation and analysis was larger than the spatial distribution variability. This was attributed to the fine sand samples from which the replicates were taken not being very homogeneous.

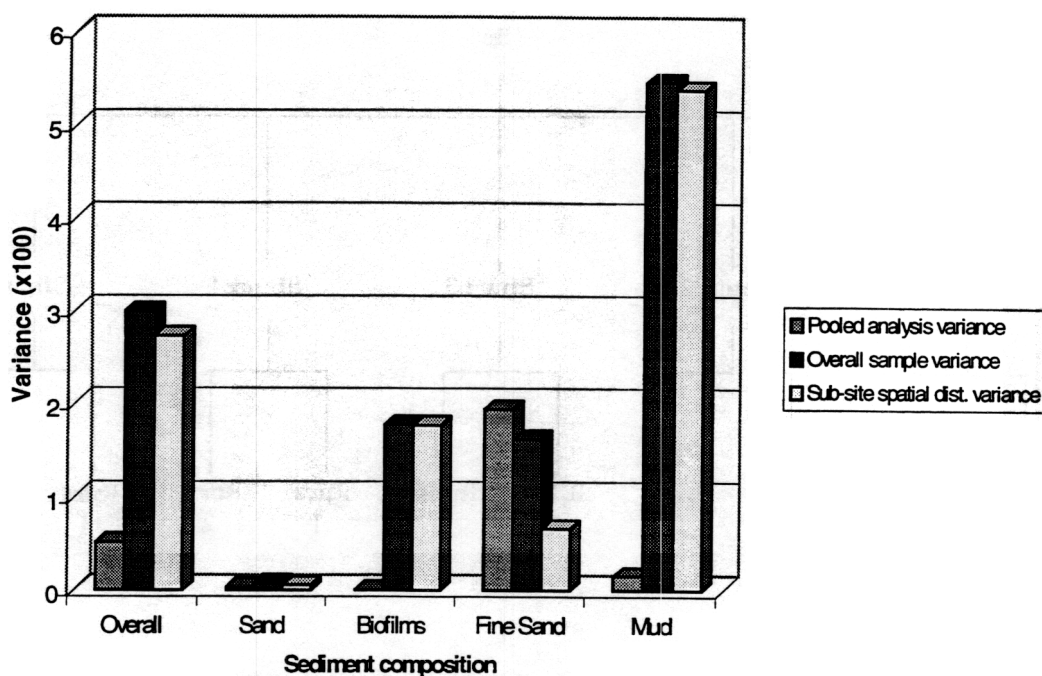


Fig. 3– Relative sizes of the sources of variability for iron sample data set

The variability associated with the preparation and analysis of the samples is also much smaller than the variability due to the spatial distribution of the sub-site samples for cobalt (Fig. 4) and manganese (Fig. 5). The variability associated with the preparation and analysis of the samples is larger than the spatial distribution variability for nickel (Fig. 6) and zinc (Fig. 7). This indicates that the nickel and zinc are more uniformly distributed across samples taken from different locations at the site. This trend is also visible in the more uniform contents of nickel and cobalt in the variety of sediment types encountered, which is discussed in the next section.

Examination of the Variance associated with the Spatial Distribution of Sediments at a Site

The variability of sample composition at a site is created by the flow patterns that occur in the river. The water velocity controls the type of depositional environment that occurs at a point. As water moves more slowly a higher percentage of fine-grained sedimentary material is deposited. This gives rise to differences in the composition of sediment samples. Biofilms cannot build up in areas where sediment is constantly being added or removed. The biofilm is either covered over by freshly deposited sedimentary material, or removed with the departing sediment. Layers of biofilm are commonly encountered in rapidly moving environments, such as sections of riffle over rock ledges. The microorganisms that form the biofilm layer actively attach themselves to the solid surface over which the water is flowing. The layer can then grow without being removed under normal flow conditions.

Many subsystems of sedimentary environments may be encountered at a site due to the processes describe above. These types of material have different average metal concentrations as well as differing degrees of variability. The mean metal

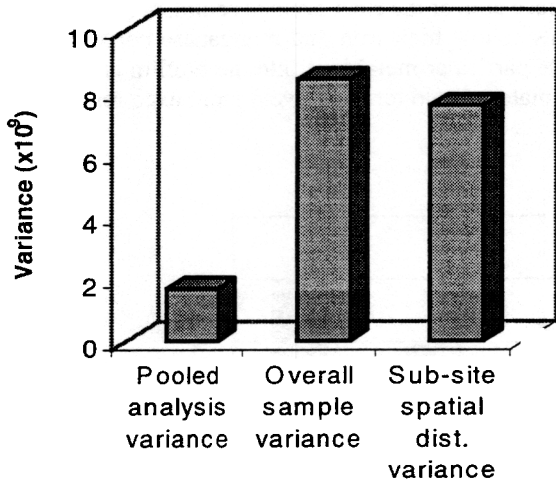


Fig. 4 - Sources of Variance for Cobalt

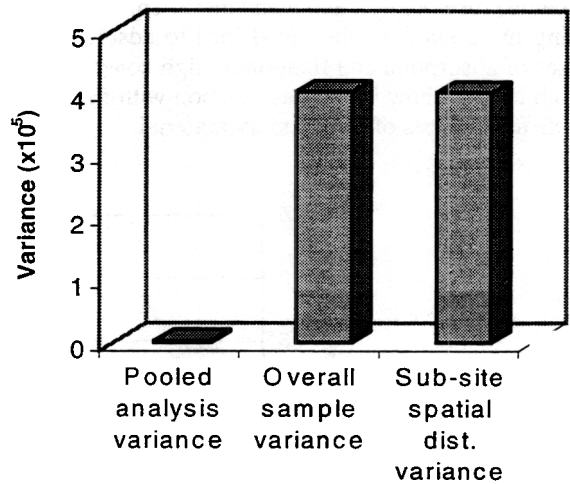


Fig. 5 - Sources of Variance for Manganese

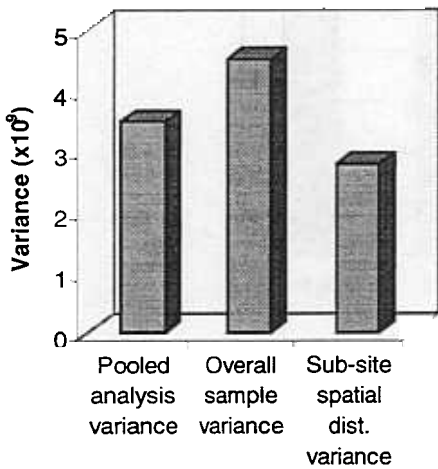


Fig. 6 - Sources of Variance for Nickel

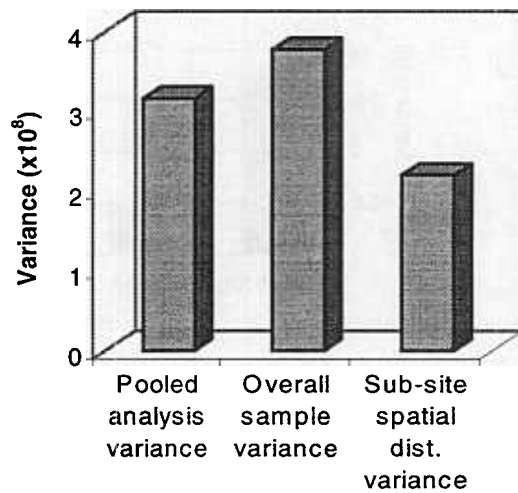


Fig. 7 - Sources of Variance for Zinc

contents of the site were calculated using the 25 values averaged from the duplicate analysis of each sub-site sample. The mean metal contents for the overall site as well as for each of the sedimentary material categories are shown in Fig. 8 to Fig. 12. There is a trend of increasing metal content as the grain size of the sediment gets smaller (ie sand→ fine grained sand→ mud) for both iron and manganese. This is because the surface area of the finer grained sediment is higher, thus providing more sites for the metal ions to adsorb to. Biofilms also show high iron and manganese contents due to the processes of absorption and fixation of high concentrations of these particular metal ions into the biofilm layer. Nickel and Zinc both tend to show highest association with fine grained sand material, and tend to have a more even range of contents for the different types of sedimentary material.

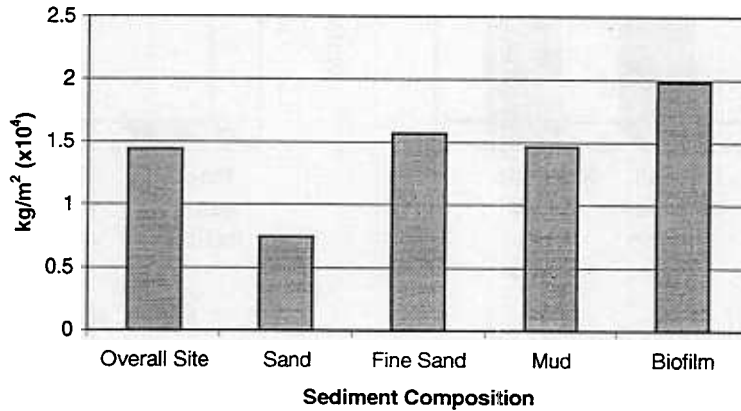


Fig. 8 – The mean Co content for the overall site and each of the sedimentary material categories

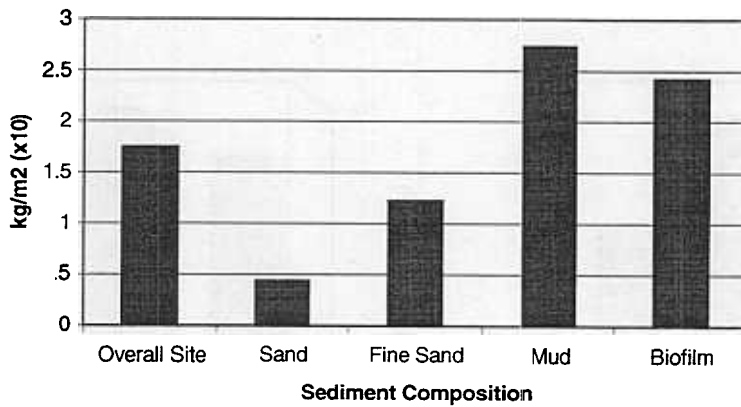


Fig. 9 – The mean Fe content for the overall site and each of the sedimentary material categories

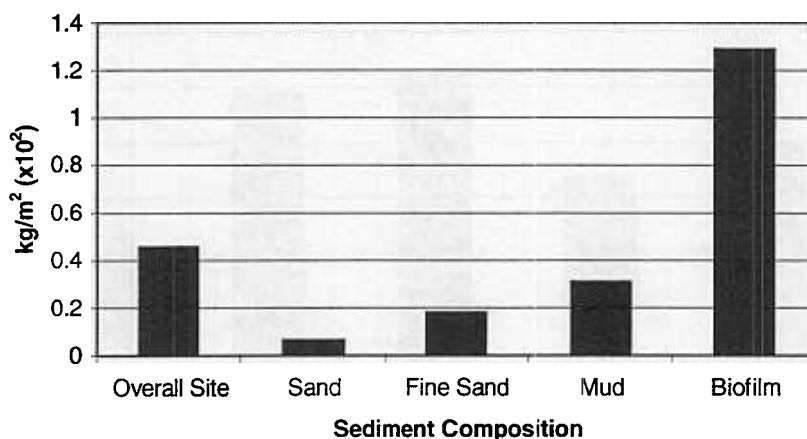


Fig. 10 - The mean Mn content for the overall site and each of the sedimentary material categories

The different types of sedimentary material encountered at a site are the main cause of variability. Variability exists between materials of the same type, but it is not generally as high as the overall site variability. This trend can be seen by comparing the spatial distribution variance of each of the categories of sediment to the spatial distribution variance of the

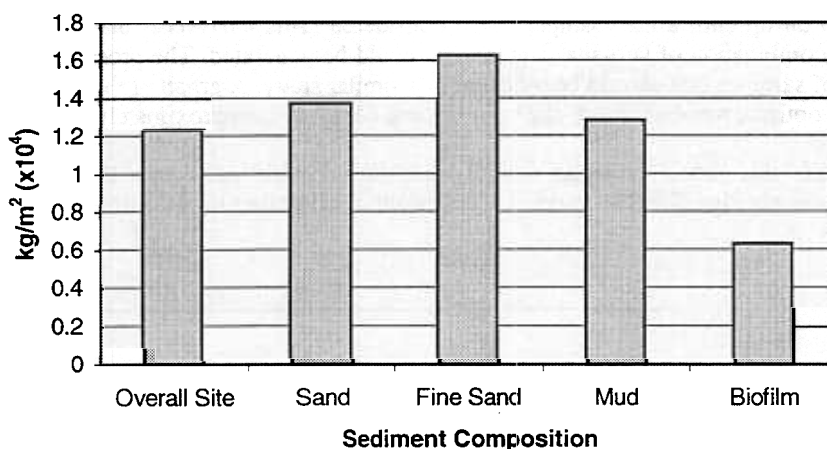


Fig. 11 - The mean Ni content for the overall site and each of the sedimentary material categories

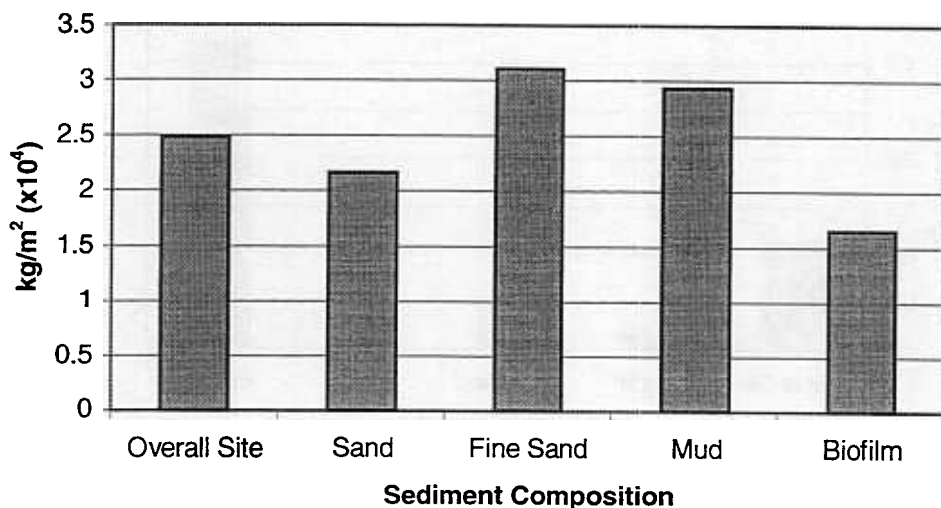


Fig. 12 - The mean Zn content for the overall site and each of the sedimentary material categories

overall site for iron in Fig. 3. Mud was the exception, showing high variability in its composition. A study of the effects of the number of sub-site samples taken on the variability of the results obtained was conducted. This involved graphing the average variability generated by 1000 random combinations of two sub-site samples, 1000 random combinations of three sub-site samples, and so on up until all 25 samples were considered. This analysis is biased by the fact that it does not consider every possible combination of sub-site samples that could be generated. The process, however, provides a rough estimate of the number of samples that should be collected in a similar study. A graph of the results of this analysis for iron is shown in Fig. 13. The optimal number of sub-site samples was found to be approximately 15.

Taking fewer samples than this generates higher overall variability. Taking more than 15 samples does not enhance the results, as the variability is not significantly lowered. This result also applied to all of the other metals considered in the study.

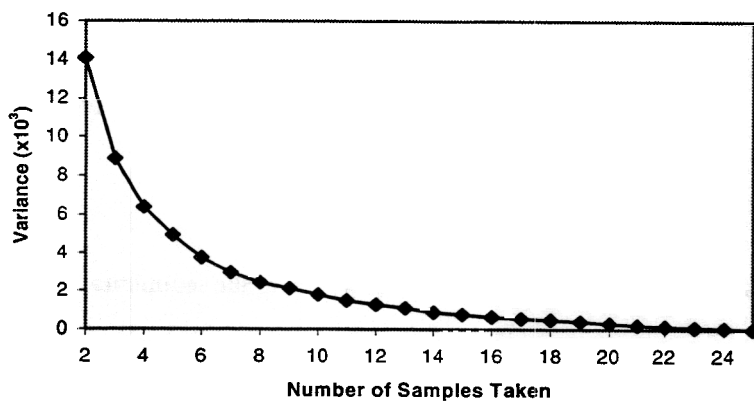


Fig. 13 - Effect of Sample Numbers on Variance in Sediment Iron Content

Composite Sampling Technique Trial

A composite sampling strategy was also explored. The value of taking a composite sample to reduce the number and volume of samples that needed to be transported back from each site and analysed was evaluated. Two composite samples were prepared by adding 10% (according to total wet sample mass) of each of the sub-site samples collected. This method ensured that the composite samples contained the same relative proportions (by wet mass) of material as was initially collected from each equal area that was sampled.

The composite samples were prepared and analysed identically to the individual samples. The masses of the specified metals in the composites were compared to the mean of the masses of the metals in the individual sub-site samples. The composite samples both yielded results within one standard deviation of the average content of the metals calculated from the analysis of the 25 sub-site samples*. This indicates that the method successfully represented the average metal content of the samples that were used to make up the composite.

The composite could be prepared in the field using a technique where equal areas of sediment from each node are combined. This composite sample would then be much easier to transport from the sampling site and would require much less analysis effort than the equivalent number of individual samples.

It should be remembered that results obtained from composites have higher levels of variability than indicated by repeated analysis of the sample. This is because the variance of the spatial distribution of the samples still exists, although it cannot be determined. The method is not suitable for determining if there are zones within a study area that exceed specified threshold values. The method is, however, suited to the determination of the average metal content within the sediment of a river at a certain location, as in the case of the regional sediment survey being undertaken here.

STUDY CONCLUSIONS

Considerable variability in metal content exists in the sediments within the immediate area of the sampling site. The main influence on the sediment metal content at any given location is the variety of sediment types and grain size that may be encountered. Variability exists at a small spatial scale and can thus influence the average metal concentration results for the site if not allowed for in the sampling methodology. To ensure that small scale spatial variability is taken into account it is recommended that about 15 sub-site samples be taken from a set sampling pattern at a site.

Positioning sampling points on the nodes of an evenly spaced grid that is randomly positioned at the sampling site reduces sampling bias, providing representative sampling of the site. The variability associated with the preparation and analysis of the samples was generally considerably less than the variation of samples due to their spatial location. The size of the spatial variability could influence the choice of analysis method employed for such a study. Highly precise techniques may not be efficient when the accuracy of the data is degraded by the site variability. Composite samples can provide the same level of metal content accuracy for a considerably reduced analysis effort.

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* except for Mn content in one composite, which fell just outside of the one standard deviation range of the average metal content

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