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A METHOD FOR THE EXTRACTION OF CARBONACEOUS PARTICLES FROM LAKE SEDIMENT

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1.0 INTRODUCTION.

Lake sediments provide a record of atmospheric contamination and so have been important in recent studies on surface water acidification. Carbonaceous particles derived from fossil-fuel combustion are found in considerable numbers in upper levels of sediment cores taken from areas with high acid deposition (Griffen & Goldberg 1981, Renberg & Wik 1984). Sites in the United Kingdom show close correlation between the onset of atmospheric contamination as indicated by carbonaceous particles, heavy metals and magnetic deposition, and the acidification of lakes as indicated by diatom analysis (Battarbee *et al.* 1988).

The particulate emissions from high temperature fossil-fuel combustion can be divided into two groups, carbonaceous particles, which are composed mainly of elemental carbon (Goldberg 1985), and fly-ash spheres, which are formed by the fusing of inorganic minerals within the fuel (Raask 1984). Of the three fossil fuels commonly used in the United Kingdom, only coal and oil produce spherical carbonaceous particles. Those produced from peat combustion have an amorphous appearance, many still retaining some cellular structure.

In order to characterise these particles into fuel type by using energy dispersive X-ray analysis (EDAX), it is first necessary to concentrate the particles to a much higher extent than that in which they occur in lake sediments. Elemental carbon is resistant to chemical attack and so unwanted fractions of the sediment can be removed by selective digestion. This paper describes previous extraction methods and proposes modifications which enable particle concentrations to be calculated with a high degree of sensitivity and precision.

2.0 BACKGROUND and PREVIOUS METHODS.

Smith *et al.* (1975), first produced a method for the extraction of elemental carbon from marine sediments. An acid treatment with hydrofluoric and hydrochloric acids was used to remove some mineral species and a basic peroxide treatment was used if organic material was present. The remaining carbon material was ground up and infra-red spectroscopy used to determine quantitatively the elemental carbon levels. This was adapted by Griffen & Goldberg (1975) for coastal marine sediments, where there was a higher organic content, and again infra-red spectroscopy was used to determine elemental carbon fluxes. This carbonaceous material was thought to originate principally from forest fires, as concentrations increased on a latitudinal basis; particles being transported by the major wind systems. However, it was also suggested that the more spherical and perforated particles might have been formed by high temperature fossil fuel combustion.

Griffen & Goldberg (1979), then turned to the freshwater sediments of Lake Michigan. The elemental carbon particles were extracted and compared against oil, coal and wood fly-ash. It was concluded that forest and grass burning could contribute a significant amount of carbonaceous material to the atmosphere, but the concentration of the "spherical" carbon particles reflected the history of fossil fuel combustion in the area. Similar results were obtained at Green Lake, New York (Kothari & Wahlen 1984), where a similar digestion technique to that of Griffen and Goldberg, was employed except that nitric acid was used to remove the organic fraction instead of basic peroxide.

Goldberg *et al.* (1981), showed that the concentration of certain trace elements such as tin, chromium, nickel, lead, copper, cobalt, cadmium, zinc and iron showed a similar profile in the sediment to carbonaceous particles. Magnetic fly-ash spherules, which were formed by the oxidation of iron minerals in the furnace to haematite (Fe_2O_3) and magnetite (Fe_3O_4), were also correlated.

Griffen & Goldberg (1983), later used sphericity and surface morphology to separate anthropogenic particles into coal, oil and wood/coal. Nine classifications were used depending on shape and surface texture of the particles. Sub-micron spherical carbon particles which had aggregated into chains (ie. soot) were extracted from Lake Michigan sediment using a similar chemical technique. These particles showed a constant concentration over the previous 40 years and were attributed to material transported over a long distance before deposition.

In Sweden, an alternative method of carbonaceous particle concentration determination was developed, using hydrogen peroxide (H_2O_2) to remove organic material, followed by direct counting of a small fraction of the residue to obtain the number of particles per gramme dry weight of sediment. This was used as an indirect dating method by matching concentration levels with that of a core previously dated by ^{210}Pb, ^{137}Cs or varve counting (Renberg & Wik 1985a). As for Lake Michigan (Griffen & Goldberg 1975, 1979, 1983; Goldberg *et al.* 1981) and Green Lake (Kothari & Wahlen 1984), the elemental carbon concentrations were found to reflect the increase of industrial activity and the fossil fuel combustion history of the twentieth century (Wik *et al.* 1986). Apart from this temporal distribution of carbonaceous particles, a spatial distribution was observed which reflected the industrial regions of Sweden. This was seen in both lake sediments (Renberg & Wik 1985b) and forest soils (Wik & Renberg 1987).

The work so far on carbonaceous particles in lake sediments in Britain, has been done using the Renberg and Wik method. The lakes involved have been principally in Scotland (Wik *et al.* 1986, Battarbee *et al.* 1988, Battarbee *et al.* in press) and Wales (Battarbee *et al.* 1988). Here also, the carbonaceous particle record follows the history of fossil-fuel burning. The record begins in the mid-nineteenth century at the time of the onset of the Industrial Revolution in Britain, and a sharp increase in concentration occurs after World War Two which reflects the expansion of the power generation industry (Darley 1985).

3.0 THE METHOD.

The aim of this work was to develop a sensitive technique, based on concentrations, suitable for use even at low carbonaceous particle numbers, by removing unwanted sediment material by selective chemical attack. Neither of the two methods in the literature were perfectly suitable for these requirements.

The Renberg and Wik method is insensitive at low particle concentrations, owing to the amount of residue left at the end of the digestion, and counting at x50 will miss particles in the <10 μm fraction.

The method used by Griffen & Goldberg (1975), deals with all charcoal, not just spherical particles produced from high temperature combustion and so the results are expressed in percent carbon by weight, rather than particle concentration. Also, only the >38 μm fraction is considered, which excludes many smaller particles and preferentially those which are oil derived. However, this method reduces 10 g of dried Lake Michigan sediment to 10-30 mg of some of the more persistent minerals, primarily pyrite (FeS_2), anatase and rutile (TiO_2) and zircon ($Zr(SiO_4)$), but most importantly elemental carbon. It involves a more complete digestion than that of Renberg and Wik and therefore is used as the basis of the method proposed here.

3.1 Laboratory procedure

1) Place 0.2 g of dried sediment in a covered 250 ml beaker.
Add 30 ml 6M KOH and 4 ml 30% H_2O_2.
Leave overnight, centrifuge at 2000 rpm for 5 minutes and then wash the residue with distilled water and return to the beaker.

This stage breaks up the sediment for further reaction and removes most of the organic and humic fractions. The use of 10 g of dried sediment and large quantities of reagents is unnecessary. As replicate digestions were to be done, an arbitrary value of 0.2 g of dried sediment was decided upon and the reagent quantities reduced to match. Griffen and Goldberg used ultrasonic dispersion to break up the sediment in the early stages of their digestion. However, carbonaceous particles are quite fragile physically and this can cause fragmentation. As Griffen and Goldberg ground up the eventual residue for infra-red analysis, this was not important, but for this study, the particles are required whole and so ultrasonic dispersion was not used. It was found that the first basic peroxide step broke up the sediment satisfactorily.

2) Add 30 ml 6M HCl to the residue.
Heat on a hotplate at 80°C for 2 hours.
When cool, centrifuge and wash as before.

This removes the HCl soluble salts, such as carbonates and bicarbonates, and removes the soluble materials which may form insoluble fluorides in the next step.

3) Transfer the residue to PTFE beakers (with PTFE lids).
Add 20 ml 40% HF and heat on a hotplate at 150°C for 3 hours.
Wash as before.

This breaks down the siliceous minerals and removes the silicon as SiF_4. The time was reduced by changing the hydrofluoric acid step from 6 days at room temperature to 3 hours at 150°C. Using scanning electron microscopy (SEM), this change showed no effect on the particles and almost halves the length of the digestion, which can now be completed in 6-7 days.

4) Return the residue to the 250 ml beakers.
Add 30 ml 6M HCl and heat on a hotplate at 80°C for 2 hours.
Wash the residue again.

This step removes any fluorides formed in step 3.

5) Add 20 ml 6M KOH and 25 ml 30% H_2O_2 in 5 ml aliquots, to the residue.
Leave overnight in an oven at 55°C. Cool and wash the residue.

6) Transfer the residue to a 25 ml beaker and add 4 ml 6M KOH and 1 ml 30% H_2O_2.
Leave overnight in an oven at 55°C. When the reaction is complete, cool and wash again.

Steps 5 and 6 remove the remaining organic and humic matter.

7) Add 10 ml 6M HCl and heat on a hotplate for 2 hours at 80°C.
Wash again. Transfer the residue to storage vessel.

Note: (i) All containers should be kept covered to stop possible atmospheric contamination. The presence of carbonaceous particles in dust shows the need for a dust free preparation room.
(ii) All supernatant fractions (after centrifuging) are discarded. (see Recovery rate).

3.2 Density separations.

Further extraction of the material by density separation was considered. However, owing to the high variability of 'apparent' density of the carbonaceous particles, this idea was discarded. Some of the carbonaceous particles have internal gas pockets with no opening to the exterior, which would give the particle a density of less than 1 g cm^{-3}. Fragmented particles and those having open structures would have the density of elemental carbon ie. 2-3 g cm^{-3} and others with varying pore sizes would have a density between these two extremes.

In addition, although the minerals remaining at the end of the digestion have a higher density than that of elemental carbon, there is a sufficiently small amount of them that it does not seem worth the extra time and potential loss of recovery to include density separation in the standard digestion technique. However, for sediments with an exceptionally high concentration of these minerals, a density separation could be used.

3.3 Filtration.

After digestion there is a great deal of fine, amorphous, black material present in some layers and this can cause problems in the counting stage by obscuring the shapes of the particles. This material does not always follow the same trends as the carbonaceous particle record as it is sometimes scarce in the surface layers. Therefore, it seems that it is not of the same origin as the particles and it has been thought it may be a precipitation product of the digestion technique itself (Renberg pers. comm.).

As it is fine material, the obvious way to remove it is by filtration. This will enable a higher fraction of the residue to be counted, increasing repeatability, as well as making counting easier. However, filtration also removes the smaller carbonaceous particles, 10 μm and 5 μm filters reducing the recovery rate to 40% and 65% respectively. As carbonaceous particles from oil combustion are usually smaller than those from coal, this approach may selectively remove oil particles from the residue, making filtration of limited use.

3.4 Effects of the method on the carbonaceous particles

In order to see the effect of the method on the chemistry and morphology of the carbonaceous particles, a sediment sample was spiked with some material from an oil- fired power station. In this way, the particle characteristics could be compared before and after digestion. Using SEM, it was seen that the digestion had no effect on particle morphology and work is now in progress using EDAX to look at possible chemical effects of the method.

3.5 Counting

A known fraction of the remaining residues were evaporated on to coverslips. These were then mounted using 'Naphrax' diatom mountant, and the whole of each coverslip counted at x400 using a light microscope. Random views were not used, as at the bottom of the particle record, where there was either one or zero particles to be counted on the whole coverslip, this raised the limit of detection. The method of adding a known amount of polystyrene microspheres and calculating the number of carbonaceous particles from the ratio (Battarbee & Kneen 1982) was found to have higher errors, especially at low concentrations.

3.6 Repeatability

To ascertain if separate digestions of a sediment sample would give the same particle concentrations, five replicate digestions from three different sediment levels were performed. This was followed by triplicate counts from each digestion. This then gives 15 concentrations for each level from which the standard deviation can be found. The results were as follows:

Level	Counts			Mean	Stan. Dev.	95% Conf. Limit
0.0 - 0.5 cm	61280	73390	69002	70073	6398	48418 - 86168
	68132	75691	74795			
	66072	70144	74501			
	55273	66379	66123			
	75273	76426	78659			
4.5 - 5.0 cm	41978	52241	40974	45947	4933	26000- 62771
	33617	45714	46427			
	45415	49764	48301			
	52027	42957	47824			
	44096	46003	51867			
11.5 - 12.0 cm	8944	8346	8469	8303	1021	3715 - 15140
	6476	7609	9606			
	8244	8886	8498			
	7429	10441	8131			
	6823	7735	8912			

As might be expected, the error increases going down the core, where fewer particles are present.

3.7 Recovery rate.

A suspension of known carbonaceous particle concentration was made up, by adding a small amount of oil-fired residue from a power station to water. After homogenisation a known fraction was then removed and counted at x400 under a light microscope. The concentration of the suspension could then be calculated. A known number of particles from this suspension were added to a sediment sample before digestion. The sediment sample was from sufficiently low down the core that it could be assumed that no carbonaceous particles were present within it. After the digestion, the number of particles was counted as before and the numbers were compared to give a recovery rate. The digestions were done in triplicate and the recovery range was from 93.9% - 100.1%, showing that very few particles are lost during the digestion. This is confirmed by taking the supernatant fraction from each stage (usually discarded) and centrifuging at 2000 rpm until a residue is deposited. Using SEM, the residue showed no particles of any size to be present in the supernatant fractions of any stage of the digestion.

Blank digestions were also done (ie. no sediment involved), to check on atmospheric contamination and cross contamination from other digestions. These showed that as long as the digestion vessels are kept covered and reasonable precautions taken in manipulating the digestion material, no atmospheric or cross contamination occurs.

One source of contamination is the smearing of surface sediments down the inside of the core tube upon coring. This pushes sediment from layers rich in carbonaceous particles down into pre-industrial depths. Carbonaceous particles have been seen in very old sediment and as these particles are not formed by any 'natural' processes, smearing seems to be the only explanation. This was tested by preparing digestions from a sediment layer just below the start of the carbonaceous particle record, (eg. 30-31cm depth in Loch Tinker - see below). Duplicate digestions were performed on the middle of the sediment slice and from around the edges. For the digestion of the internal slice, only one particle was found in four separate counts, but particles resulting in a concentration of about 200 particles g DW^{-1} were counted on the samples from the exterior. This shows that smearing does take place, and at lower levels within the carbonaceous particle record could have a significant effect on particle number calculations, demonstrating the need for 'trimming' core slices, ie. using sediment from the interior of the core only.

3.8 Detection limit.

The Renberg and Wik method, removing as it does, only the organic fraction from the sediment, leaves a large amount of material at the end of a digestion. Therefore, unless a very long time is spent counting each sample, only a small fraction of the residual material will be counted and hence the limit of detection is quite high (ie. if only 1 particle is counted in the residual sample fraction, the result is a value of 80-100 particles per gramme dry weight.

Using the method described above, the material remaining after digestion is predominantly carbonaceous. Therefore, at the bottom of the core, very little material remains and if so desired, 100% of this material could be counted in a fairly short space of time. As approximately 0.2 g of dried sediment is used for the digestion, if only 1 particle is counted, this will give a detection limit of approximately 5 particles per gramme dry weight, at least a ten-fold improvement on the other method.

4.0 APPLICATION TO A SEDIMENT CORE.

The method described was applied to a sediment core taken from Loch Tinker in the Trossachs region of central Scotland. The carbonaceous particle record has previously been counted using the Renberg and Wik method so a comparison between the two methods can be drawn. The core was also dated using ^{210}Pb and the results are shown in Figure 1.

The basic trends are the same for both methods (ie. the carbonaceous particle record begins in the early 1800s and there is a large rise in concentration after the 1940s).

As a higher percentage of the digested material is available to be counted all the way up the core, particle counts are higher and the accuracy improved. By using a higher magnification (x400 as opposed to x50 in the Renberg and Wik method) the smaller carbonaceous particles down to 1 µm are included. Below this size the settling velocities of such particles are very small indeed, especially compared to wind velocities and so deposition will be reduced. Using x40 and x50 magnification, only particles down to 5-10 µm can be counted (Renberg & Wik 1984, 1985a, 1985b; Wik & Renberg 1984, 1987; Darley, 1985). Because of this, particle concentrations at the top of the core are higher than those of the Renberg & Wik method. Lower down, at and below the point where the limit of detection for the Renberg & Wik method is reached, the particle concentrations become lower, due to the better sensitivity of the method described here. This is best illustrated in an expanded bottom section of the graph, (See Figure 2). Consequently, there is no single factor by which it is possible to convert the numbers obtained in one method to that of the other, without redigesting and recounting the material.

Figure 1. Comparison of the Two Methods of Extraction using Loch Tinker Sediments

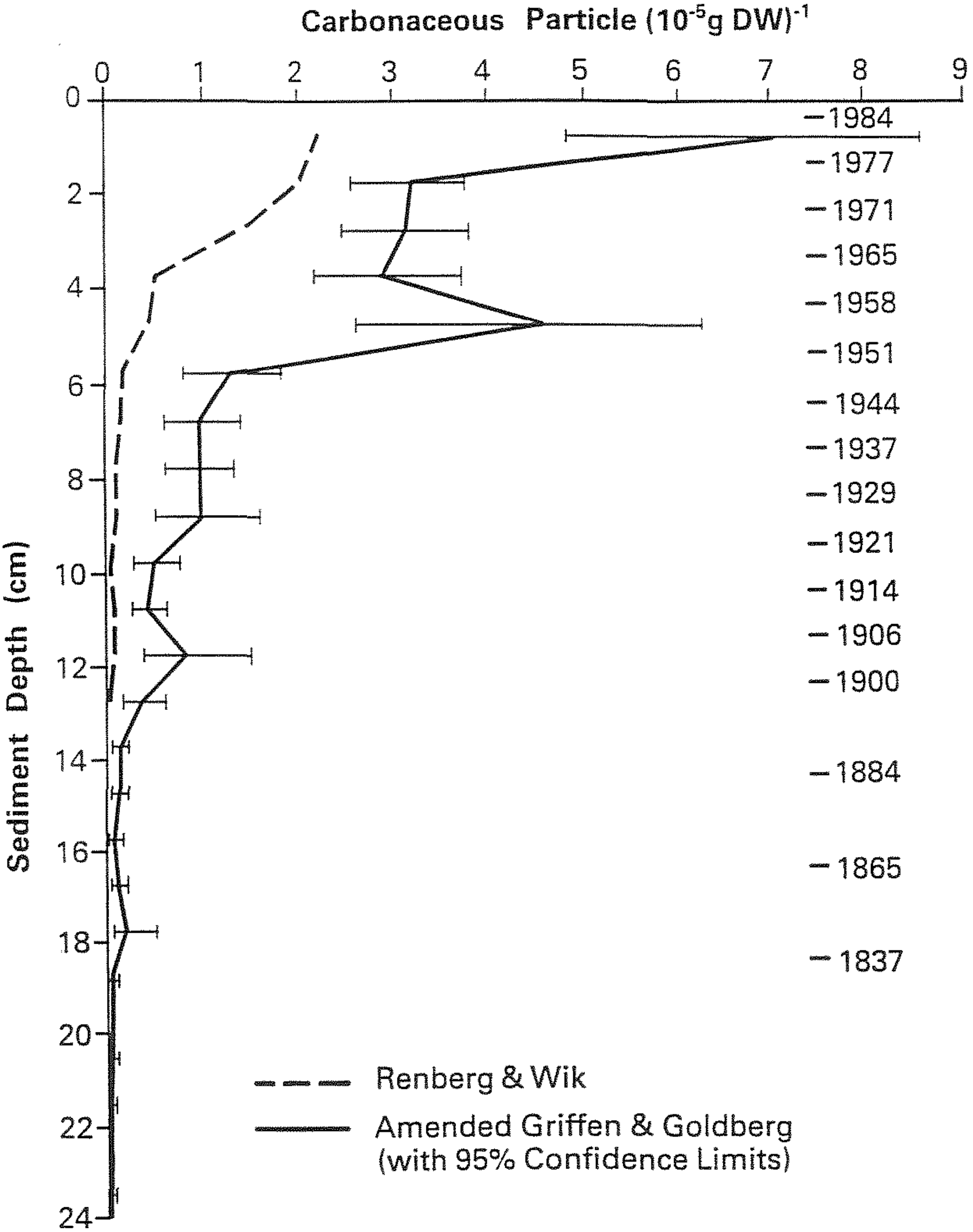
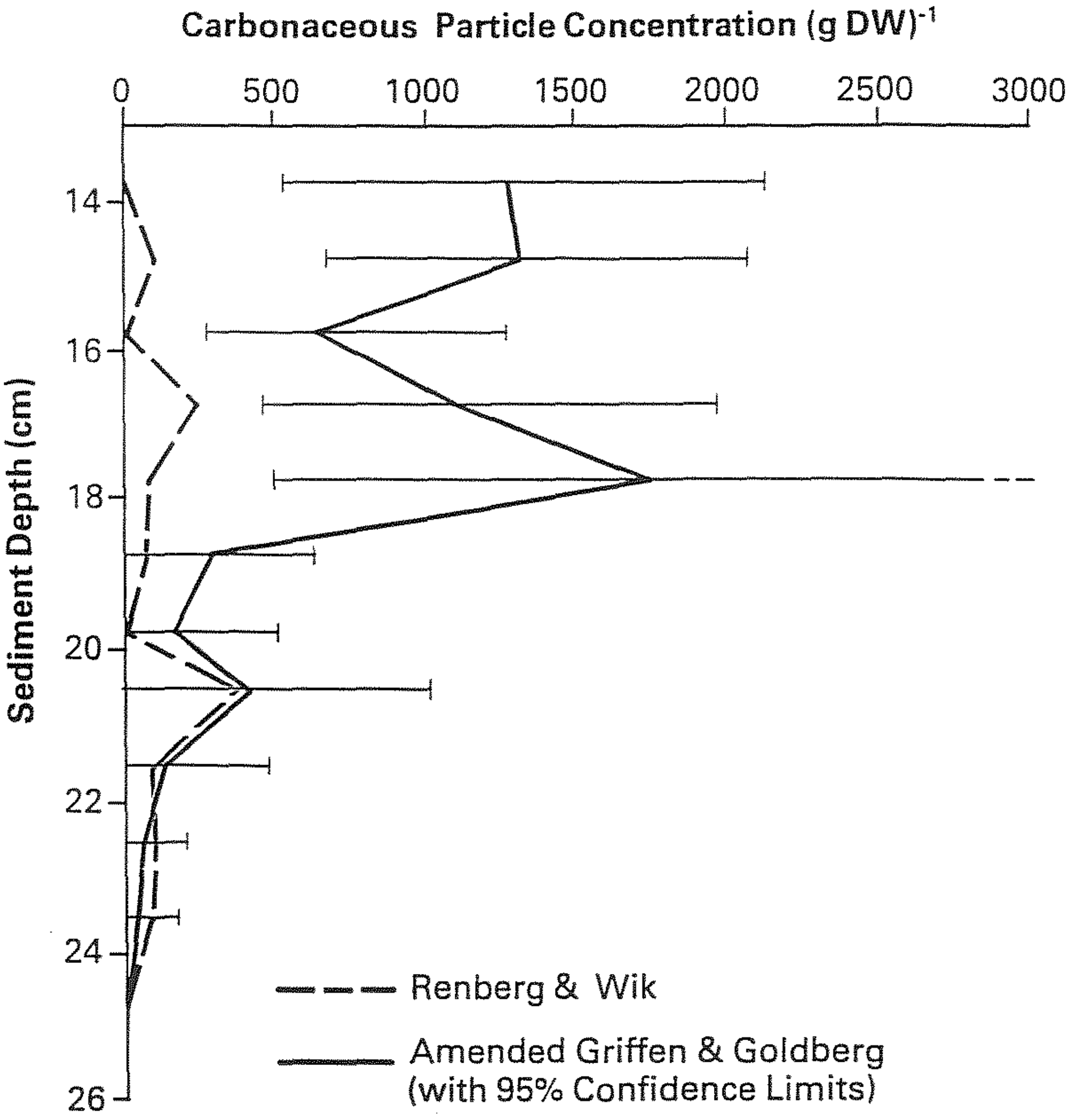


Figure 2. Expanded Bottom Section of the Loch Tinker Profile to Compare Detection Limits of the Two Methods



5.0 CONCLUSIONS

The method described above, has a number of advantages over previous methods used to extract carbonaceous particles from sediments. It is more accurate and has a lower detection limit than the Renberg and Wik method previously used on British lakes, and it is quicker and involves less risk of fragmentation of the particles than the Griffen and Goldberg method upon which it is based.

Although the majority of the residue at the end of the digestion is carbonaceous material, the extraction is not perfect and some minerals survive, albeit in low concentrations. This includes some silicates, and even one or two siliceous spheres may appear in the residue, due to particles being washed in from the beaker walls after the HF digestion step. This is not particularly important as the remaining non-carbonaceous material is sufficiently different both chemically and morphologically, that the counting and EDAX procedures will not be confused by their presence.

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