Diatom Dissolution in Saline Lake Sediments An Experimental Study in the Great Plains of North America

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Abstract

Environmental reconstructions are limited by the quality of the original data from which they are derived. In situations where microfossils are poorly preserved problems may arise, both through taxonomic uncertainty and more subtly from the alteration of the death assemblage as a result of the differential robustness of species. Diatom dissolution tends to be a particular problem in saline lakes.

Laboratory-based dissolution experiments on fresh, modern diatoms collected from lakes in North and South Dakota and Saskatchewan were carried out to establish the abundance and composition changes of assemblages as dissolution progressed. Analysis of experimental results demonstrates that species exhibit regular dissolution relationships and can be ranked according to susceptibility to dissolution. Changes in valve morphology for selected key taxa were categorised under scanning electron and light microscopy into "dissolution stages". These data provide the basis for developing dissolution indices for individual taxa and assemblages, which can be related to absolute abundance changes of diatom valves.

Experimental data were applied to two separate weighted averaging (WA) transfer functions to predict measured dissolution parameters (such as dissolved silica) and to a salinity transfer function developed from the Northern Great Plains. In the former case, models incorporating dissolution stage counting were more accurate and robust (as validated by jackknifing).

Species and samples were downweighted according to species robustness (dissolution rank) within the WA transfer function. Downweighting either, or both, species and samples in the transfer function algorithm lead to minor improvements in model performance in terms of both r^2 and standard error (as RMSE), despite incomplete coverage of species. A short core from Spiritwood Lake, North Dakota, was used to test the differences variable weighting had on reconstructed salinity. Results suggest Spiritwood Lake is only responsive to more extreme climatic events, and has remained fresh (<0.5g/l TDS) or subsaline (0.5-<3g/l TDS) throughout the last 150 years. The approach of variable sample and species weighting to the rest of the NGP surface sediment assemblage training set may improve the model further, which could be tested at sites with an historical record of salinity.

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Abstract

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Notation used in Chapter 5

r_i Mikkelsen's diatom resistance index (Mikkelsen 1980)

a_1 Resistance ranking based on the average rank position (r_i) for a species

a_2 Resistance ranking derived from ordering a_1 values

Both a_1 and a_2 values can be adjusted according to the total sum of ranks within an assemblage.

β Average values of r_i scores

β' β values divided by the sum of **r** values over all samples in each assemblage

β'' Ratio of sum of **r** values for a taxon (r_i) to the sum of all **r** values for all taxa in an assemblage

***A*-rank**

Standardisation of taxon β values according to the β value for *Amphora libyca* for each assemblage

DDI_x ("Flower's DDI")

Dissolution index based on ratios of pristine to dissolved valves in a sample developed from ideas in Flower & Likhoshway (1993)

W Diatom dissolution index incorporating weighting by dissolution categories ("stages")

W^2 Diatom dissolution index weighted by the square of dissolution stages

Chapter 1
Introduction

1.1 Introduction

On a global basis, saline lakes are important inland waters, and although unevenly distributed, occur on every continent. Almost as great a volume of continental water is saline (104,000 km^3) as fresh (125,000 km^3; Vallentyne 1972). Despite this abundance much less is known about the physical, chemical and biotic aspects of these systems compared to freshwater lakes. This may be because saline lakes are often more remote than freshwaters, predominantly in arid and semi-arid zones (Williams 1981). However, saline lakes can be important sources of mineral salts, nutrients and energy (Friedman & Krumbein 1985).

Interest in, and research on, saline lakes has grown in the twentieth century (e.g. Clarke 1924, Beadle 1932) especially in relation to mineral extraction and fishery potential. In the last twenty years the value of saline lakes as sensitive indicators of environmental, and particularly climatic, change has been recognised (*e.g.* Street & Grove 1976, Last & Schweyen 1985, De Deckker 1981). In common with freshwater lakes, saline lake sediments contain a record of the local and regional environment to a sub-annual resolution at sites where varves occur. Saline lakes are often the best, and perhaps only, sources of palaeoenvironmental information in semi-arid and arid areas (Bowen 1985, COHMAP 1988).

1.2 Definitions of inland saline lakes

Saline lakes are defined here as those with a total dissolved solids concentration (TDS) of 3g/l or over, which is a major ecological threshold for many biotic groups although these boundaries are permeable (Williams 1981, Hammer 1986; table 1.1). From an ecological perspective, there is a fundamental difference between saline lakes derived from marine and those from continental environments for which the "brackish" or "marine" terminology is inappropriate (Por 1972, Bayly 1970, Moore 1987). Brackish water is characterised by an ionic composition similar to that of seawater, and more importantly has a marine ecology which is halotolerant rather than salt tolerant, implied by early halobien classifications (*e.g.* the diatom systems of Kolbe 1927, Hustedt 1953 & 1957). To avoid this ambiguity, Bayly (1967) suggested the terms "thalassic" for those mainly coastal waters with a marine ecology and "athalassic" for continental waters. Although athalassic as an adjective refers to surface inland water of any salinity, its use has narrowed and now implicitly refers to inland saline waters.

Table 1.1 - A classification of saline lakes (after Hammer, 1986)

Category	Salinity (g/l TDS)
freshwater	<0.5
subsaline	0.5-<3.0
hyposaline	3.0-<20.0
mesosaline	20.0-<50.0
hypersaline	≥50.0

Athalassic lakes are generally associated with arid and semi-arid climatic belts, although some, in areas of moisture surplus, are related to geologic salt deposits or anthropogenic salinization of surface waters (Hammer 1986). Athalassic lakes vary from deep, perennial lakes to shallow, ephemeral playas and these extremes divide athalassic environments into separate systems from both a sedimentological (Last 1983, Last and Schweyan 1983), and ecological viewpoint (Hammer 1986).

Salts enter the lake itself either in precipitation directly, or more importantly as surface or subsurface inflows of soil and rock water, altered in salinity and composition from precipitation through chemical reactions over time. Reaction with basic minerals in rocks, such as calcium or magnesium carbonates, or silicates, is a vital step in determining the pathway of eventual "brine evolution" which is mainly achieved through evaporative concentration (Garrels & Mackenzie 1967, Eugster & Hardie 1978). Globally, freshwaters are carbonate-bicarbonate systems while most saline waters are Na/Ca/Mg-SO_4/Cl/CO_3. Lakes within the same geological region tend to share the same dominant ionic composition, for example lakes within the East African rift valley (Na-CO_3/Cl/SO_4; Hammer 1986), in Australia (NaCl; Williams 1981) and in the Northern Great Plains of America (Na/Mg-SO_4; Last 1989, Last 1991). Within these broad confines there is, however, considerable spatial and temporal heterogeneity.

Salinity variability (poikilosalinity) over time and space is an important feature of inland saline lakes, in terms of both total salinity and ionic composition (Begin et al. 1974, Moore 1987, Eugster and Hardie 1978, Timms 1976, Last 1989). The seasonal cycles of Saskatchewan lakes are typical of continental, high altitude or high latitude lakes. A spring meltwater dilution is followed by summer or autumn evaporative concentration, and a winter ice layer which concentrates salts according to the relative thickness of ice to water depth (Rawson and Moore 1944, Moore 1952, Hammer 1984).

Profound changes in water level and salinity may lead to the deposition of salts which are not quickly redissolved when lake levels rise again, or which may be removed from the catchment by natural, or human, agency from exposed lake bottoms (Langbein 1961). This hysteresis has been observed in Devils Lake after the 1930s drought and in the refilling of Lake Eyre in 1973 and 1974 (Dulhunty 1977). Langbein (1961) estimated the time taken for various lakes to acquire their contemporary salt loads, varied from 800 years (Devils Lake), to 5,500 years (Lake Eyre), to 30,000 years (the Dead Sea), and proposed a "salt cycle" involving the hysteresis of lake volume and salinity.

Variations in salinity of individual lakes over longer time periods, or changes in the spatial distribution of saline lakes, can be used to infer climate change, although the response of any

given lake will depend on its precise hydrological and hydrogeological regime (De Deckker & Forester 1988). Saline lake palaeolimnology of sensitive sites has an important role in elucidating moisture balance fluxes in arid and semi-arid regions.

1.3 Saline lakes in environmental reconstruction

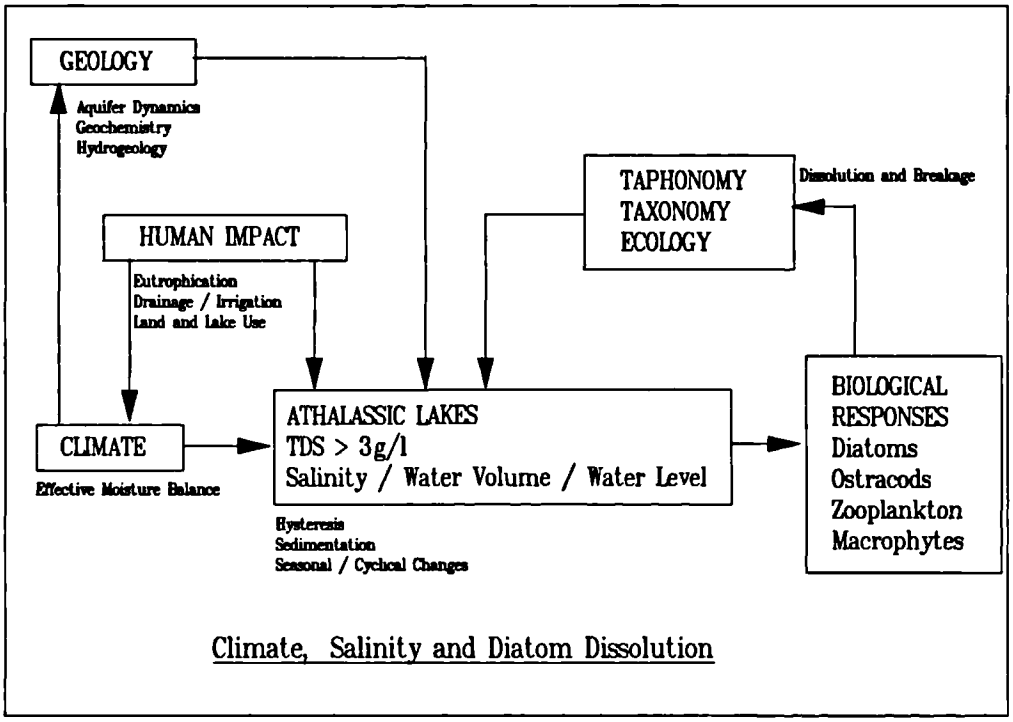
1.3.1 Lakes in environmental reconstruction

Lake sediments often provide a record of local and regional environments which have great potential for accurate palaeoenvironmental reconstruction at a high spatial and temporal resolution (Smol 1990, Battarbee 1991). Biological microfossil remains in particular can yield detailed information of the lake and its surroundings, from both autochthonous and allochthonous sources, of primary producers (including diatoms, chrysophytes, pollen and spores) and consumers (notably molluscs, ostracods and chironomids; Anderson & Battarbee 1994).

Fresh and saline lakes tend to respond with different sensitivity to components of their environments, particularly with respect to climatic change. Freshwater lakes with a positive water balance (precipitation in excess of evapotranspiration) do not accumulate dissolved solids, and remain dilute open systems, but may be linked to climate through responses to temperature change, to which biota may respond (Delorme *et al.* 1977, Zeeb & Smol 1993). Saline lakes are often closed basins (endorheic) in areas where evapotranspiration exceeds precipitation. Changes in temperature and precipitation affect lake water balance, and are reflected in lake volume and salinity changes (De Deckker & Forester 1988). Figure 1.1 is a schematic representation of the links between climate, water balance and salinity in closed basins. The reconstruction of salinity from biological or geochemical evidence from saline lake sediments can be used to infer past lake volume and climate change, although the relationship may be blurred by processes including salinity hysteresis and taphonomy. Microfossil preservation is often a particular problem in saline lake sediments.

Lake level fluctuations have been used as proxies for climatic change in many closed basins both within and beyond the tropics (Street & Grove 1976, Street-Perrott & Roberts 1983, Street-Perrott & Perrott 1990, Gasse *et al.* 1987, Harrison *et al.* 1988). Patterns of synchronous regional lake level variation can be used to test global circulation models (Kutzbach & Street-Perrott 1985, Spaulding 1991) which provides an important means of model validation.

Figure 1.1



Climate, Salinity and Diatom Dissolution

1.3.2 The palaeolimnology of saline lakes

A systematic palaeolimnology of saline athalassic lakes has only really developed in the last two decades, as an understanding of both saline geochemistry (Last 1984, Last 1989) and ecology has developed (Hammer 1986). Research has focused on the late Quaternary palaeolimnology of athalassic saline lakes in Central and South America, East and North Africa, the western United States and Canada, and Australia, using geochemical, sedimentological and biological data for increasingly quantitative reconstruction of environmental parameters. In the last decade there has been a growing amount of research associated with global climatic change in the wake of international concern about global warming. Quantitative empirical studies are needed to test the hindcasts of models as a means of estimating reliability of forecasts (Kutzbach & Guetter 1986, Schweger & Hickman 1989, Engstrom & Fritz 1989).

Fine resolution palaeolimnological techniques have been used to reconstruct the more recent histories of saline lakes in Morocco (Stevenson & Battarbee 1991) and the United States (Bradbury 1988, Fritz 1990, Fritz *et al.* 1994) and at crucial times during the late Quaternary (Roberts *et al.* 1993).

There has been considerable interest in the palaeolimnology of saline lakes in the mid-western United States and Canada for over twenty years (Watts and Wright 1966, Watts and Bright 1968, Haworth 1972). Recent studies of late Pleistocene/Holocene environmental change have been made at Walker Lake, Nevada (Bradbury *et al.* 1989), Baptiste Lake, Alberta (Hickman *et al.* 1990) and Ceylon Lake, Saskatoon (Last 1990). Over the last ten years an important regional dataset covering the Northern Great Plains (North and South Dakota, and southern Saskatchewan) has been built up which is developing transfer functions for quantitative salinity reconstruction, using both diatom and ostracod records (Fritz & Battarbee 1988, Jacobson & Engstrom 1989, Radle *et al.* 1989, Fritz 1990, Fritz *et al.* 1991, Fritz *et al.* 1993).

Diatoms are abundant, sensitive, and taxonomically identifiable often to species level or below. Diatom analysis has been applied to environmental reconstruction of pH (Gasse & Tekaia 1983, Charles & Smol 1988, Battarbee 1990, Battarbee & Renburg 1990), eutrophication history (Hall & Smol 1988, Anderson *et al.* 1993, Bennion 1994) and salinity (Juggins 1992, Cumming & Smol 1993). Ecological knowledge has improved through recent systematic accounts of the diatom flora in east and north Africa (Richardson 1968, Richardson & Richardson 1972, Hecky & Kilham 1973, Gasse *et al.* 1983, Gasse 1986, Khelifa 1989), South Africa (Schoeman & Archibald 1976-80), North America (Patrick & Reimer 1966, 1975) and Australia (Gell & Gasse 1994).

Diatom analysis has been a widely used method in saline lake palaeolimnology, in central and south America (Bradbury 1971, Bradbury *et al.* 1981, Van der Hammen *et al.* 1981, Watts and Bradbury 1982, Bradbury 1989), Africa (Gasse *et al.* 1987, Gasse *et al.* 1989, Flower *et al.* 1989, Barker 1990, 1992) and North America (Haworth 1972, Fritz 1990, Fritz *et al.* 1991, Fritz *et al.* 1993). Diatom preservation can be problematic, particularly in high alkalinity, high pH systems.

Ostracods have been used to infer environmental parameters such as salinity, in similar ways as diatoms (Delorme 1989, De Deckker & Forester 1988). In addition, the shells of individual species can be used in stable isotope analysis of both trace metals and $\delta^{18}O$ ratios (Lister *et al.* 1991), and ^{14}C (AMS) dating (Colman *et al.* 1990). The shell calcite of ostracods incorporates trace amounts of metal ions exchanged for calcium ions in the lattice, principally the related Mg^{2+} and Sr^{2+} ions. These are found in strict ratios with shell Ca^{2+}, according to the ratio of the trace metal to Ca^{2+} ions in the water in which the ostracod grows, although the Mg^{2+}/Ca^{2+} partitioning coefficient is also temperature dependent (Chivas *et al.* 1985, Engstrom & Fritz 1989). These ratios are related to the total salinity of the water in a more complex fashion, as at a given ionic ratio there is a range of corresponding salinity values, depending on the particular route of evaporitic concentration, which in turn depends on the original brine type (Eugster & Hardie 1978, Engstrom & Fritz 1989). Nevertheless, there is much scope for complementary diatom-ostracod analysis, especially as different processes are necessary to degrade calcite and silica in sediments.

As research into and knowledge of other biogenic and inorganic techniques increase, other underused fractions of core material could be found to be environmentally diagnostic and complement other interpretations. Chrysophyte cysts, for example, are common in shallow, oligotrophic lakes, and tolerate higher salinities but their value is only just beginning to be recognised (Sandgren 1991, Cumming *et al.* 1993). This holistic approach is especially important in saline lake palaeolimnology where environmental information in the sediment record is often less than perfectly preserved for many biotic groups.

1.3.3 Saline lake taphonomy

1.3.3.1 Taphonomic processes

Taphonomy describes the suite of processes that transform a living community (biocoenose), to a death assemblage (thanatocoenose) and finally a fossil assemblage (taphocoenose). Preservation and destruction of biogenic matter in lake systems vary between different biotic groups, and between different limnological conditions. Saline lakes share many taphonomic

similarities with freshwater systems but often create special taphonomic problems of their own.

Sediment deposition and accumulation vary across lake basins, depending on lake morphometry, mixing in the water column, sediment slumping, and resuspension episodes (DeNicola 1986, Anderson 1990) which may lead to incomplete sedimentary records (McKinney 1991). In saline lakes, water levels may vary on a seasonal, annual or longer timescale, and sedimentary records may be far more variable in spatial extent and temporal coverage. Periodic and aperiodic desiccation is a feature of athalassic lakes, and may lead to the erosion of sediment from the catchment. The intrusive growth of salt crystals in subsurface brines during playa conditions may confuse stratigraphic profiles both physically and chronologically (Last & Schweyan 1983).

Lake level changes also influence vertical mixing profiles. Laminated deposits may form in saline lakes in the absence of sediment mixing, through turbulence or bioturbation, although such laminations may be associated with aperiodic (Neev & Emery 1967) or periodic events (Roberts *et al.* 1993).

Microfossil representation in lake sediments is affected by factors including type and proximity to source communities (Bradbury & Winter 1976, DeNicola 1986, Cameron 1990), delivery to sediments (in faecal pellets for example, Conway *et al.* 1977, Goddard & Hoggett 1982, Blome & Albert 1985, Haberman 1985, Turner 1991) and preservation (Livingstone 1984, Noël & Bunson 1986). The differential preservation both between and within taxonomic groups is of crucial importance in palaeoecology and environmental reconstruction from biogenic remains.

The conditions under which organic matter, carbonates, pollen and silica are preserved in lakes are complex and incompletely understood. Pollen and organic matter tend to be poorly preserved in oxic environments (Faegri & Iversen 1975, Roberts *et al.* 1993, Livingstone 1984, Wilding *et al.* 1977), while carbonates are prone to dissolution in acidic freshwaters (De Deckker & Forester 1988). Though silica dissolution has been recognised in freshwaters (Round 1964) it is a particular problem in the high pH waters of saline lakes.

1.3.3.2 Diatom preservation in saline lakes

Diatom silica dissolution is a potential problem in all lake and sediment environments but only becomes a major problem in situations where either, or particularly both, parameters of dissolution rate and reaction time are high. This predisposes many saline lakes with high pH to dissolution problems (Krauskopf 1982) but occurs in situations where low specific kinetic

rates of dissolution acting over extended time periods (Schelske *et al.* 1983, Glover 1982, Flower 1993). Where diatoms sediment over large distances in undersaturated water, or can dissolve in sediments where pore water silica levels cannot be maintained at saturation levels, dissolution can be the dominant taphonomic process.

The relationship between meromixis and diatom dissolution is unclear. Meromixis is a condition in which part of the lake fails to circulate over the long term (Walker & Likens 1975). The upper, mixed layer (mixolimnion) behaves almost as a separate unit in the system and may thermally stratify, but the bottom layer, the monimolimnion, is chemically different from the mixolimnion and separated from it by well-defined chemical (chemocline), density (pycnocline) and temperature (thermocline) discontinuities. Several studies have reported poor diatom preservation in the monimolimnion (Merilainen 1971, 1973) and appreciable silica dissolution under anaerobic conditions (Kato 1969). Evidence also exists for reduced dissolution in the presence of organic matter (Lewin 1961, Hinman 1990), which would itself be preserved under anoxic conditions in the monimolimnion (Hecky & Kilham 1973). Under anoxic conditions, bacteria (*Desulfovibrio* and *Desulfotomaculum*) are largely responsible for the reduction of oxides associated with negative redox potentials (E_h). Common products include FeS (Post 1977) and H_2S (Eugster & Hardie 1978). Breakage from bioturbation will be reduced under such conditions (Huc 1988).

Sedimentary diagenetic alteration of biogenic silica may produce authigenic silicates, which can in themselves be evidence of dissolution episodes related to environmental change in the lake hydrogeochemistry (Stoffers & Holdship 1975, Singer & Stoffers 1980). Authigenic smectite has been observed on diatom frustules in saline lakes (Badaut & Risacher 1983) and living marine diatoms (van Bennekom & van der Gaast 1976). Silica reprecipitation has been noted to occur on both frustules (Mikkelsen 1977, Barker 1994) and sediments (Flower 1993) at concentrations of dissolved silica below saturation level.

Destructive processes do not necessarily end once a sample has been collected. Recent research (Flower 1993, Hodgkinson 1991) has demonstrated that standard techniques for microfossil preparation may bias assemblage composition and sample preservation outside the natural taphonomic environment.

1.3.3.3 Diatom dissolution in lakes of the Northern Great Plains

Diatom and ostracod assemblages from the surface sediment of the 55 lakes in the Northern Great Plains dataset have been used to build transfer functions to quantitatively reconstruct salinity histories of individual lakes in the region (Fritz 1990). Such reconstructions can be

tested against known historical values where these are found, as at Devils Lake, North Dakota, and have been found to correspond well to salinity records below values of about 10 g/l TDS. Periods of higher salinity are distinguished from those of lower values, but the reconstructed salinity underestimates the highest salinity excursions over about 16-18 g/l TDS while overestimating those at about 10-15 g/l TDS (Fritz 1990, Fritz *et al.* 1991).

A possible explanation for this asymmetrical performance, as far as the diatom-based reconstruction is concerned, may be in the diatom record itself, rather than in the analytical method used in the construction of the transfer function (Fritz *et al.* 1991). The differential preservation of diatoms in both the water column and within the sediment could bias the fossil assemblage to those taxa that are most resistant and robust, which will in turn bias the reconstructed environmental variables (in this case salinity) towards the optima of those taxa. The transfer function may itself be affected by preservation bias in the surface sediment samples, and so the training set.

In order to test the hypothesis that differential dissolution susceptibility does have an effect on the transfer function, the fact of differential preservation of diatom taxa must be established and, as far as possible, quantified. Dissolution experiments can provide insight into the relationship between taxa in terms of relative dissolution rank. Furthermore, the extent to which the dissolution of assemblages and individual taxa can be measured by sequential changes in valve morphology can be explored, and quantified in terms of observed dissolution parameters.

1.3.3.3 Applications of preservation studies

Dissolution can severely affect microfossil assemblages and the ability to make reliable and accurate palaeoecological or palaeoenvironmnetal inferences from them (Sherrod et al 1990).

Approaches to microfossil preservation in a marine context have centred on foraminiferal, coccolith, diatom and radiolarian dissolution from both a qualitative and quantitative, experimental viewpoint (*e.g.* Berger 1968, Berger *et al.* 1982, Be & Anderson 1976, Peterson & Prell 1985, Johnson 1974, Erez *et al.* 1982, Thompson 1976 & 1981, Thunell & Honjo 1981, Shemesh *et al.* 1989, Pichon *et al.* 1992). Dissolution indices have been used to demarcate dissolution zones within sediments which are correlated with glacial-interglacial cycles affecting dissolution rates (Thompson & Saito 1974, Farrell & Prell 1989). Diatom dissolution is often an extremely significant component of silica cycling in aquatic systems (Gouleau & Noel 1984, Dickson 1975).

The increasing use of multivariate statistical techniques in palaeoecology (Birks 1985, Birks *et al.* 1990) has allowed quantitative reconstructions of dissolution parameters derived from

empirical experiment (Pichon *et al.* 1992). The effect of microfossil dissolution also has implications for transfer functions reconstructing ecological parameters from microfossil assemblages (Hutson 1977, Hutson 1978).

1.4 Objectives

The object of this study is to assess the importance of differential dissolution as a taphonomic process that alters the death assemblage, and the development of techniques to reduce the distortion of environmental information that the assemblage represents. Valve fragmentation and breakage, though important (Beyens & Denys 1982), are not the focus of inquiry, though the two are in practice difficult to separate. In high pH lakes, dissolution is considered the dominant cause of poor preservation (Fritz *et al.* 1991, Barker 1992, Barker et al 1990).

Processes of non-destructive taphonomic alteration are not considered in this study. Experimental results will only be applied to the surface sediment assemblage, as it is this sample that is the basis for palaeoecological study. Extrapolating the relationship between this assemblage and the living diatom flora of a lake is not simple, as it takes into account aspects as diverse, and difficult to evaluate, as diatom productivity and standing crop, and physical processes of sediment erosion, transport and deposition within the lake environment. This is not to deny the importance or value of these features limnologically but purely in terms of palaeoecological utility the surface sediment is a valid representation of the whole lake environment (Anderson & Battarbee 1994). The reconstitution of the surface sediment death assemblage is justifiably an end in itself as a basis for environmental reconstruction.

1.5 Structure of thesis

Chapter 2 describes the environment of saline lakes in the Northern Great Plains, including study sites. Diatom sampling and preparation methods are considered in Chapter 3. A methodology for controlled dissolution of fresh diatom material is developed in Chapter 4, which is applied to material collected from lakes in the Northern Great Plains in 1991 and 1992 in Chapter 5.

The results of these experiments are analysed quantitatively in Chapters 6 and 7, using multivariate statistical techniques to analyse experimental data. In Chapter 6, transfer functions, based on the weighted averaging method, are developed to assess the prediction of measured dissolution parameters (dissolved silica) from experimental data, comparing the results when dissolution state of valves is included in the analysis. The experimental data on species ranking are used to variably weight samples and species and applied to a previously developed transfer

function for reconstructing salinity in lakes from the Northern Great Plains of America and tested on a short core from Spiritwood Lake, North Dakota in Chapter 7.

Chapter 2
The Northern Great Plains study area

2.1 Introduction

The Northern Great Plains (NGP) is the term given to a loosely defined physiographic region of the central plains of North America, and roughly comprises the states of North and South Dakota in the United States, and the southern parts of the adjacent Canadian states of Saskatchewan, Alberta and Manitoba (figure 2.1, from Fritz *et al.* 1991). The area is characterised by flat to rolling surface topography of generally low relief and low elevations rising from east to west. The large numbers of lakes, marshes and other wetland that have developed on hummocky glacial till throughout much of the field area also gives rise to the name "prairie pothole region".

2.2 Environmental setting of the Northern Great Plains

2.2.1 Study sites

Potential evapotranspiration is currently in excess of precipitation on an annual basis throughout the region, and this deficit in effective moisture increases from north-east to south-west (figure 2.1). Lakes and surface waters in this region exhibit a wide range of salinity, and ionic composition, reflecting this moisture trend and variations in catchment soils, geology and human impact (Bright 1968). The NGP lake dataset includes 64 lakes covering a salinity gradient of 0.7-270 g/l, of which 55 contain diatoms in the surface sediments (shown in figure 2.1) and for which limnological data are summarised in table 2.1 (from data in Fritz *et al.* 1993).

Generally, lakes in the NGP can be classified as high pH, sodium/magnesium sulphate systems (table 2.1). There is considerable variation even amongst the major ions (at least 20% of the total cation or anion sum), with both carbonate (Elbow and Shinbone) and chloride (Reflex) lake types represented, which may itself lead to differences in the diatom flora at the same salinity (Fritz 1990). Conductivity mirrors salinity particularly at lower values (Hem 1982). Six lakes in the dataset are meromictic (Medicine, Redberry, Sayer, Basin, Waldsea and Deadmoose). Not every lake includes all habitats, for example the development of a planktonic flora may be restricted in shallow lakes, while the littoral zone is highly variable in extent and character amongst the lakes (Chapter 3).

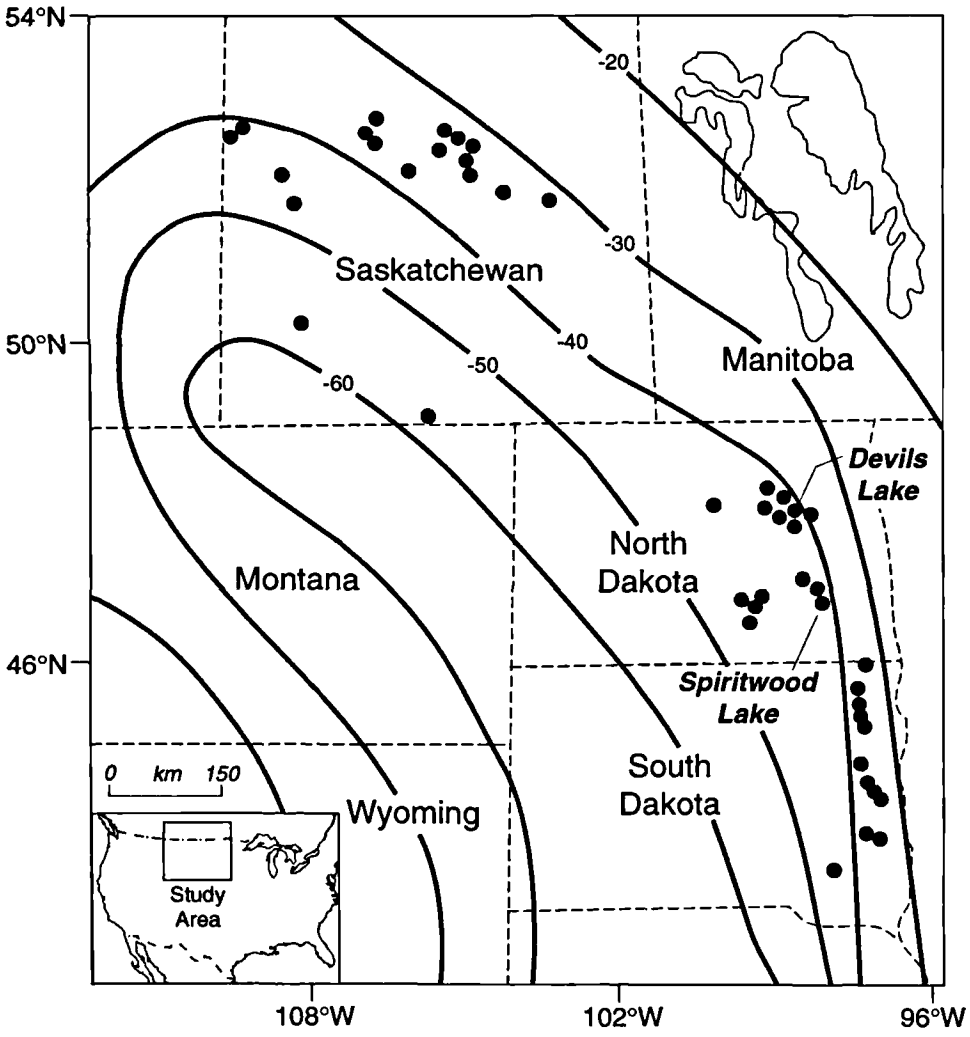


Fig. 2.1 The Northern Great Plains of America

The contours show net annual moisture balance (precipitation, **P**, less potential evapotranspiration, PE_t) in centimetres.

Table 2.1 - Study sites in the NGP (from Fritz *et al.* 1993)

No.	Site name	County	State	Location		Major ions (decreasing abundance)		Sample depth (m)	pH	Cond. (µS/cm)	Salinity (g/l)
				N lat.	W long.	Cations	Anions				
1	Albert	Hamlin	S.D.	44° 32'	97° 09'	Mg(Ca)	$SO_4(CO_3)$	1.6	8.7	850	0.71
2	Alkali	Sargent	N.D.	46° 02'	97° 23'	Na	$SO_4(Cl)$	2.6	9.1	7350	6.08
3	Basin	Saskatchewan		52° 38'	105° 17'	Mg(Na)	SO_4	11.3	8.9	19600	21.21
4	Bitter	Day	S.D	45° 17'	97° 19'	Mg(Na)	SO_4	0.1	9.2	21000	23.53
5	Boucher	Saskatchewan		52° 28'	105° 41'	Mg(Na)	SO_4	0.8	8.8	4350	3.94
6	Big Quill	Saskatchewan		51° 55'	104° 22'	Mg(Na)	SO_4	2.4	8.9	33300	37.91
7	Byron	Beadle	S.D.	44° 33'	98° 10'	no data	no data	1.3	---	2777	2.20
8	Coldwater	McIntosh	N.D.	46° 01'	99° 04'	Mg(Na)	$SO_4(CO_3)$	9.0	8.6	3800	3.52
9	Coon	Nelson	N.D.	47° 58'	98° 23'	Na(Mg)	$SO_4(CO_3)$	1.3	8.3	1950	1.63
10	Deadmoose	Saskatchewan		52° 19'	105° 10'	Na(Mg)	$SO_4(Cl)$	28.0	9.0	25800	21.50
11	Devils	Ramsey	N.D.	48° 05'	98° 56'	Na(Mg)	$SO_4(CO_3)$	7.0	8.8	3500	2.76

Table 2.1 (contd.) - Study sites in the NGP (from Fritz *et al.* 1993)

No.	Site name	County	State	Location		Major Ions (decreasing abundance)		Sample depth (m)	pH	Cond. (µS/cm)	Salinity (g/l)
				N lat.	W long.	Cations	Anions				
12	Eckelson	Barnes	N.D.	46° 56'	98° 17'	Na(Mg)	SO_4(Cl)	0.5	9.0	41300	41.41
13	East Coteau	Saskatchewan		49° 03'	104° 33'	Mg(Na)	SO_4	5.4	8.7	6350	6.94
14	East Devils	Ramsey	N.D.	47° 57'	98° 43'	Na(Mg)	SO_4	6.5	8.8	11800	9.90
15	Elbow	Benson	N.D.	47° 55'	98° 43'	Na(Mg)	CO_3	1.3	9.2	1900	1.77
16	Fife	Saskatchewan		49° 14'	105° 53'	Na(Mg)	$CO_3(SO_4)$	2.5	8.9	3800	3.41
17	Fishing	Saskatchewan		51° 51'	103° 33'	Mg(Na)	SO_4	10.8	8.3	3600	3.45
18	Free People	Benson	N.D.	47° 56'	98° 43'	Na	$SO_4(CO_3)$	3.1	9.2	11950	8.92
19	George	Kidder	N.D.	46° 45'	99° 30'	Na	SO_4	24.3	9.2	23300	21.24
20	Hazelden	Day	S.D.	45° 31'	97° 28'	Mg(Na)	SO_4	0.1	8.9	30200	35.97
21	Herman	Lake	S.D.	44° 00'	97° 10'	Mg(Ca)	$SO_4(CO_3)$	1.7	8.8	1000	0.81
22	Horseshoe	Eddy	N.D.	47° 53'	98° 48'	Na	$SO_4(CO_3)$(Cl)	2.9	9.2	7950	6.33
23	Humboldt	Saskatchewan		52° 09'	105° 06'	Mg	SO_4	6.0	8.4	2800	2.60

Table 2.1 (contd.) - Study sites in the NGP (from Fritz *et al.* 1993)

No.	Site name	County	State	Location		Major ions (decreasing abundance)		Sample depth (m)	pH	Cond. (µS/cm)	Salinity (g/l)
				N lat.	W long.	Cations	Anions				
24	Isabel	Kidder	N.D.	46° 49'	99° 44'	Na(Mg)	$CO_3(SO_4)$	1.9	9.3	2800	2.53
25	Lenore	Saskatchewan		52° 30'	104° 59'	Mg	$SO_4(CO_3)$	7.5	8.3	1050	0.89
26	Long	Benson	N.D.	48° 01'	99° 17'	Na(Mg)	$SO_4(CO_3)$	2.2	8.6	2500	2.13
27	Madison	Lake	S.D.	43° 57'	97° 00'	Mg(Ca)	$SO_4(CO_3)$	2.9	8.3	1150	0.94
28	Medicine	Codington	S.D.	44° 49'	97° 21'	Mg	SO_4	9.2	8.9	27900	38.58
29	Mission Bay	Benson	N.D.	48° 01'	98° 53'	Na(Mg)	SO_4	1.0	8.8	27200	24.37
30	Moon	Barnes	N.D.	46° 51'	98° 10'	Na(Mg)	$SO_4(CO_3)$	11.5	9.2	6850	5.81
31	Norden	Hamlin	S.D.	43° 35'	97° 12'	Mg(Ca)	$SO_4(CO_3)$	1.5	8.4	1050	0.85
32	Oakwood	Brookings	S.D.	44° 26'	96° 58'	Mg(Ca)	$SO_4(CO_3)$	1.8	8.3	800	0.68
33	Opuntia	Saskatchewan		51° 48'	108° 34'	Na	SO_4	1.5	8.5	7400	6.29
34	Piyas	Marshall	S.D.	45° 35'	97° 20'	no data	no data	1.6	---	3164	3.00
35	Poinsett	Hamlin	S.D.	44° 32'	97° 05'	Mg(Ca)	$SO_4(CO_3)$	3.1	8.3	1100	0.87

Table 2.1 (contd.) - Study sites in the NGP (from Fritz *et al.* 1993)

No.	Site name	County	State	Location		Major ions (decreasing abundance)		Sample depth (m)	pH	Cond. (µS/cm)	Salinity (g/l)
				N lat.	W long.	Cations	Anions				
36	Porter	Saskatchewan		52° 12'	106° 17'	Na(Mg)	SO_4(Cl)	0.3	9.6	6150	5.05
37	Rabbit	Saskatchewan		52° 36'	107° 00'	Mg(Na)	SO_4	4.8	8.6	7450	7.67
38	Redberry	Saskatchewan		52° 43'	107° 09'	Mg(Na)	SO_4	13.3	8.9	16800	18.92
39	Reflex	Saskatchewan		52° 40'	109° 58'	Na	Cl	9.8	9.2	12000	8.08
40	Roslyn Pond	Day	S.D.	45° 31'	97° 26'	Na(Mg)	SO_4(Cl)	2.0	9.0	4850	3.84
41	Round	Benson	N.D.	48° 02'	99° 16'	Mg(Na)	$SO_4(CO_3)$	2.2	8.6	1950	1.28
42	Round	McHenry	N.D.	48° 02'	100° 18'	Na	CO_3	5.7	9.0	3000	2.64
43	Roy	Marshall	S.D.	45° 43'	97° 27'	Mg	$SO_4(CO_3)$	3.8	8.8	2400	2.06
44	Sayer	Saskatchewan		52° 34'	105° 24'	Mg	SO_4	4.6	8.6	14800	18.75
45	Shinbone	Benson	N.D.	47° 51'	98° 42'	Na	CO_3(Cl)	1.5	9.1	3150	2.70
46	Spring	Benson	N.D.	47° 57'	98° 49'	Na(Mg)	SO_4	2.2	8.7	5650	4.84
47	Spiritwood	Stutsman	N.D.	47° 05'	98° 35'	Na(Mg)	$SO_4(CO_3)$	13.4	9.0	2550	2.03

Table 2.1 (contd.) - Study sites in the NGP (from Fritz *et al.* 1993)

No.	Site name	County	State	Location		Major Ions (decreasing abundance)		Sample depth (m)	pH	Cond. (µS/cm)	Salinity (g/l)
				N lat.	W long.	Cations	Anions				
48	Stink	Stutsman	N.D.	46° 52'	99° 24'	Na(Mg)	SO_4	1.5	9.4	28900	26.68
49	Stink	Benson	N.D.	48° 13'	99° 16'	Na	SO_4	1.2	8.5	20400	17.67
50	Tramping	Saskatchewan		52° 08'	108° 47'	Na	SO_4	4.3	9.0	13700	11.14
51	Twin	Benson	N.D.	47° 58'	99° 06'	Na(Mg)	$SO_4(CO_3)$	1.9	8.8	2000	1.70
52	Wakaw	Saskatchewan		52° 40'	105° 35'	Mg(Na)	SO_4	9.5	8.3	3050	2.88
53	Waldsea	Saskatchewan		52° 17'	105° 12'	Mg(Na)	SO_4(Cl)	11.2	8.7	21400	20.48
54	Waubay	Day	S.D.	45° 24'	97° 26'	Mg	SO_4	0.5	8.6	11100	12.24
55	West Stump	Nelson	N.D.	47° 55'	98° 26'	Na(Mg)	SO_4(Cl)	0.9	9.3	14300	11.09

2.2.2 Surface and bedrock geology

The topography and surface geology of most of the NGP to the north of the Missouri River can be read as a story of glacial advance and retreat over the Quaternary. The Missouri Escarpment, a morainic deposit, divides the drift prairie to the east from the Coteau du Missouri to the west (Swanson *et al.* 1988, Winters 1963). It separates the relatively low-lying, flat drift prairie (at altitudes of about 430m to 490m above sea level) from the hummocky topography of the Missouri Coteau, varying from about 550m to over 640m at the western boundary. The escarpment itself provides the greatest relief in the region, where surface elevations rise from east to west by 60m-90m over just a few kilometres. Appreciable relief in the drift prairie generally only occurs where rivers cut down into the plain, for example the James River, in eastern North Dakota.

2.2.3 Natural vegetation of the Northern Great Plains

Natural vegetation patterns tend to parallel changes in effective moisture and temperature regimes. Four broad ecotones are recognised at present dividing the region into the grasslands of the prairie in the driest areas to the south and west, and three forest zones (Webb *et al.* 1983). The deciduous forest adjacent to the prairie is separated from the true boreal coniferous forests of the north and east by a mixed boreal and broad-leaved deciduous forest (the "aspen parkland" of Schweger & Hickman 1989, Hickman *et al.* 1990). The aspen parkland is characterised by broad-leaved deciduous species such as trembling aspen (*Populus tremuloides*), balsam poplar (*P. balsamifera*), birch (*Betula papyrifera*) and willow (*Salix* spp.), together with some spruce (*Picea mariana* and *P. glauca*; Hickman *et al.* 1990). The northern hardwoods, such as maple (*Acer* spp.), basswood (*Tilia* spp.), oak (*Quercus* spp.), elm (*Ulmus* spp.) and ash (*Fraxinus* spp.) are also found in this zone and are joined by hickory (*Carya* spp.), walnut (*Juglans* spp.) and cherry (*Prunus* spp.) in the true deciduous forest which replace the coniferous species (Webb *et al.* 1983).

Such divisions are broad generalisations as within each ecological type may be found representatives of several others, depending on local conditions of moisture, topography and biogeography. While boundaries between the forest types are generally floristic, that separating the prairie from the deciduous forest is often quite abrupt, and on a large scale coincides with the position of natural barriers to the spread of prairie fire (Webb *et al.* 1983). Both forest and prairie species can be found in suitable habitats on both sides of the boundary, and within the prairie, deciduous trees often occur around lake margins (Bright 1968).

Most of the saline lakes in the region are found today within the prairie, north of the Missouri River, due to the extensive deposits of glacial sediments creating large areas of unintegrated, confused drainage and the subsequent lack of sufficient surface runoff since the retreat of the ice to produce coherent drainage.

Within the grasslands, several different types of floral and faunal associations exist, all of which contribute to the ecological unity of the prairie. The tall-grass prairie consists of true tall grasses such as big bluestem (*Andropogon geradi*), switchgrass (*Panicum virgatum*), Canada ryegrass (*Elymus canadensis*) and Indiangrass (*Sorghastrum nutans*), as well as some mid-grasses and grass-like plants of similar height, and forbs (such as *Ambrosia*, *Artemisia* and *Chenopodium*; Kannowski 1979, Webb *et al.* 1983). The natural range of the tall-grass prairie is in the moister areas of the plains, to the east. In drier areas, mixed-grass prairie developed, comprising of both short and medium height grasses and many species of forbs, often in clumps rather than the sods of the tall-grass prairie (Kannowski, 1979). The driest areas, such as hill tops and slopes were dominated by blue grama (*Bouteloua gracilis*) and buffalo grass (*Buchloe dactyloides*).

Deciduous woodlands within the prairie are confined to those near freshwater, such as along lake shores, valley bluffs and streambanks (Kannowski 1979, Bright 1968). In this respect valley systems such as the James River are particularly important not only as rare habitat but as migration routes linking the prairies with eastern deciduous forests of Minnesota and the Missouri River.

Wetlands are integral parts of the prairie ecosystem and are hydrologically very important as areas for groundwater recharge, discharge or both, roles which change over time (Swanson *et al.* 1988), and are sources of biological richness and diversity. Areas of endorheic or arheic surface drainage are a feature of till deposits, associated with either thin stagnant ice or retreating glaciers (Winters 1963). Stagnant ice, ablating slowly with limited meltwater available for channel formation, leaves a landscape with many depressions and relatively great relief. This contrasts with the ridges of morainic deposits left by orderly retreating glaciers, in which meltwater channels blocked by glaciofluvial sediments are natural lake or wetland sites (such as Spiritwood Lake). Such an interpretation has been made for the Coteau du Missouri (stagnant ice) and the drift prairie (active ice) in Stutsman County by Winters (1963), and the far greater prevalence of wetland in the Coteau than the drift.

2.2.4 Groundwater

The role of groundwater dynamics to surface water systems is of great importance in a region

such as the Northern Great Plains where atmospheric inputs are annually exceeded by losses through evapotranspiration. Where lakes within identical climatic ranges experience differences in the permanence, salinity and chemical composition of orders of magnitude, it must be accepted that groundwater constitutes an important, but largely unmeasured, aspect of the hydrological system. Swanson *et al.* (1988) cite several examples of lakes divided by roads or railway tracks that develop substantially different chemistries in each part of the divide, depending on groundwater flows. The influence of groundwater on lake levels and chemistry is controlled by aquifer permeability and relative topographic location within the drainage basin (Almendinger 1990), and is dynamic in both a spatial and temporal dimension (Arndt & Richardson 1993).

A comprehensive study of regional and local groundwater dynamics is beyond the scope of this study, but the recognition of its role is an important first step. Subsurface aquifers can act as sources and sinks of both salts and water from surface waters, and respond as any element in the hydrological system to changing conditions of input and output, such as climatic changes at the surface. The timing of the response is lagged in both space and time, which adds further complexity to the system and to the problem of inferring one element (climate) from the changes in another (lake salinity). Climate affects the whole hydrological system but surface lake waters are only one part of that system, under the influence of subsurface flows themselves modulated by climate. LaBaugh *et al.* (1987) found that in the Cottonwood Lakes area of Stutsman County, the dominant control of wetland chemistry was position relative to the groundwater flow structure, moderated by seasonal evaporative concentration.

2.2.5 Human impacts on the natural environment

Arguably mankind has only had a significant impact on the environment of the prairie since the arrival of the first European settlers in the nineteenth century. Archaeological evidence of human occupation for about the last 8,000-10,000 years in the Northern Great Plains has suggested that the arrival of humans from Siberia preceded the loss of several large mammals by perhaps two millennia. These include those known to have been hunted (such as the woolly mammoth, *Mammuthus primigenius*, and Jefferson's mammoth, *Mammuthus jeffersonii*) as well as native species of camel (*Camelops* spp.) and horse (*Equus* spp.) (McEvedy 1988, Graham *et al.* 1987). Over the last 5000 years, many smaller mammals have experienced as great a contraction in range and abundance as the better-known megafauna (Semken 1983).

While it is likely that human activity did have at least an indirect effect on these extinctions, climatic and environmental changes were altering the distribution and extent of habitats and viability of certain ecosystems throughout the Holocene. The human use of fire, for example,

undoubtedly had important environmental consequences, and human activity was no doubt partly responsible for the loss of such species as *Bison occidentalis* during the Holocene, but the impact of mankind entered a different phase in the 1800s. Prior to the occupancy of the plains by European settlers such environmental impacts were essentially within the scope and bounds of natural changes in scale and rate, in stark contrast to those after this time. Several megafauna suffered sharp declines in range, such as wapiti, bear, bighorn sheep, wolf and pronghorn, and the extinction of the passenger pigeon and near-extinction of the American bison are well known (Semken 1983).

It has been estimated that there were about 100,000 Horse Indians in the Northern Great Plains and somewhere between 25 to 50 million bison (McEvedy 1988). Concomitant with the destruction of the great herds of bison (*Bison bison*) towards the end of the 1800s, and the decline of the native populations of Plains and Horse Indians on whom they depended, the prairie sod was broken and converted to arable land.

Soils under the tall-grass prairie are generally amongst the most fertile of the grasslands, and as they tend to be associated with areas of low relief and more reliable precipitation (at least when the plains were being extensively settled) few tracts remain. Between 1850 and 1920, most of the natural grasslands in the eastern Dakotas were ploughed up, and the process continues (US Fish & Wildlife Service 1978). Very little pristine prairie remains as those remnants are often grazed or mown for hay (Kannowski 1979).

Together with the cultivation of the prairie, there has been considerable loss of wetland by direct draining and diversion, and by indirect groundwater alterations as a direct consequence of human activity, quite apart from other natural causes. Another part of the explanation for the greater concentration of wetland in the Coteau region may be the greater value of drained ("reclaimed") land in the drift prairie. It has been estimated that between 20-40% of the wetland in the prairie pothole region have been extensively modified or lost (in Kannowski 1979). There is protection of wetland now under US law, and increasing numbers coming under the control of federal, state and private organisations (both from voluntary contributions and revenue from hunting licences and hunting equipment taxes, for example).

The effect of removal of the natural grassland and the drainage of large areas of wetland has been a lowering in the water table on a local and regional scale (Kannowski 1979) and alteration of the groundwater system (Swanson *et al.* 1988), involving recharge and discharge sites and flow pathways. Natural grassland cover afforded protection to topsoil from erosion and increased infiltration to the subsurface, as a source of groundwater recharge. A greater proportion of precipitation enters wetland systems as runoff, and carries more sediment to

surface waters. Additives to soils and crops, such as fertilizers, insecticides and pesticides, and other farm and domestic wastes, are transported in this runoff to wetland and other habitats (Sauer 1987, 1988). Their accumulation in biotic systems adds to problems of natural ecosystems directly and indirectly as individual organisms and their habitats are affected. The cultural eutrophication of surface and subsurface waters is one increasingly common result of the experience of 20th century settlement of the prairies.

2.3 The environmental setting of Spiritwood Lake, North Dakota

2.3.1 Introduction

Spiritwood Lake in eastern North Dakota was chosen as a site to reconstruct salinity using a transfer function developed from the NGP dataset of 55 lakes (Fritz & Battarbee 1988, Fritz 1990, Fritz *et al.* 1991, 1993). The response of Spiritwood Lake can be compared to that of Devils Lake, North Dakota, which is a terminal closed basin with different hydrological and limnological characteristics. Site sensitivity can be calibrated against the observed climatic history of the last 100 years in the Northern Great Plains. Sites with different sensitivities and thresholds to change can be used to compare relative magnitudes of past environmental change, by the extent to which these are recorded in lake sediments. Regional signals from a suite of such calibrated lakes can be disentangled from local catchment events if records can be synchronised.

2.3.1 Local geology and groundwater

Stutsman County lies to the east of central North Dakota, and is approximately bisected north to south by the Missouri Escarpment (figure 2.2). The surface deposits in Stutsman county are almost all of glacial till, generally silty clays, except for fluvial silts, sand and gravel along river valleys and some areas of outwash gravel and sand to the west. The Pierre formation, which is generally shale, underlies the glacial drift at depths varying from under 30m in the drift prairie in the east to over 152m in the Missouri Coteau in the west. Almost as great a thickness fills a large buried bedrock valley in the south-est of the county, which forms the geological setting for the Spiritwood aquifer, of some importance to local and regional groundwater dynamics.

The Spiritwood Valley aquifer is an important component of both local and regional hydrology (Swanson *et al.* 1988, Huxel & Petri 1963, 1965). The aquifer is located in glacio-aqueous deposits in a buried bedrock valley cut into relatively impermeable Cretaceous Pierre shale, overlain by till where the total Quaternary deposits are over 130m in places.

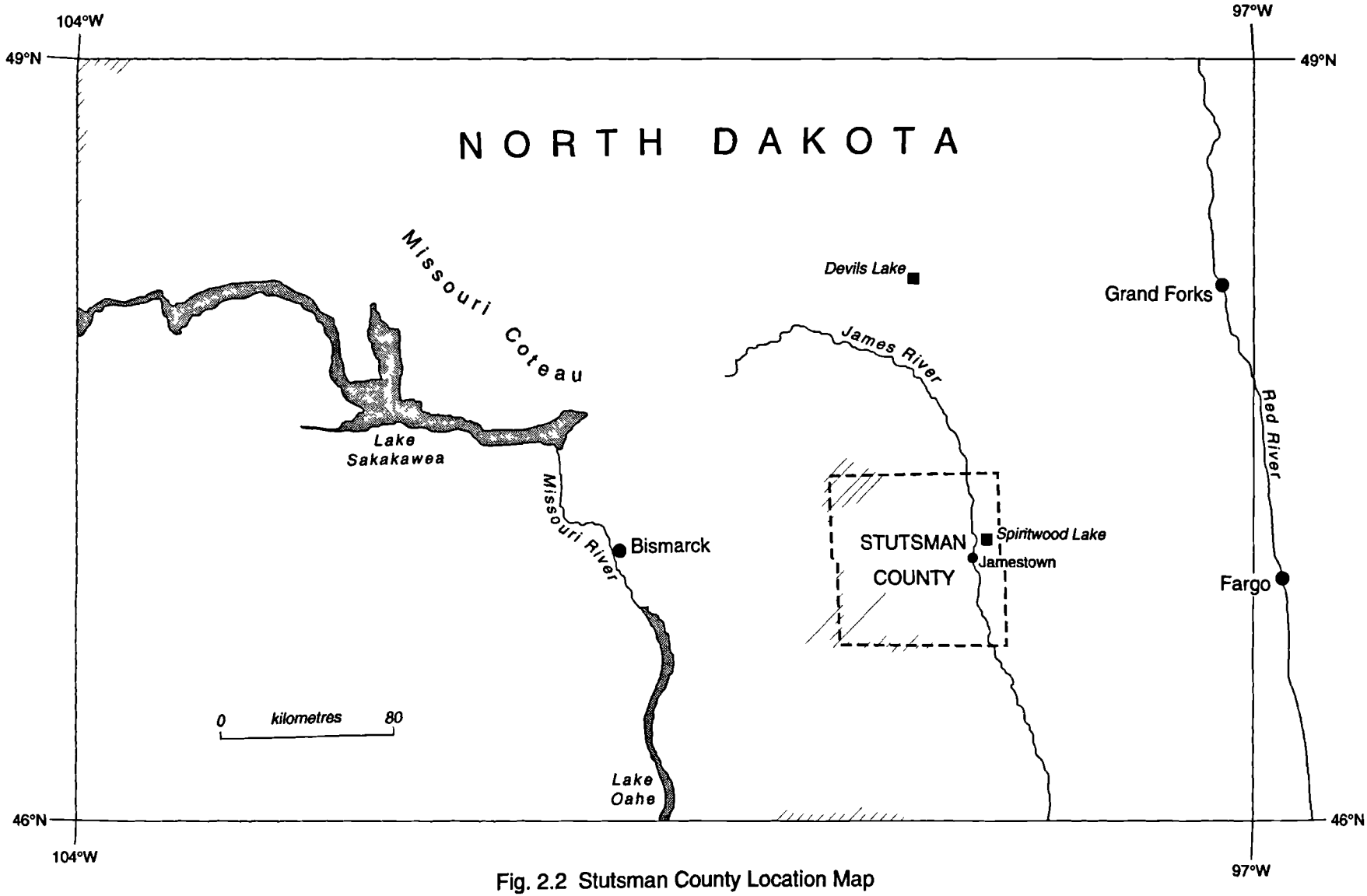


Fig. 2.2 Stutsman County Location Map

2.3.2 Stutsman County climate

Climate is typical of the continental interior, extreme in terms of temperature with the bulk of the precipitation falling over the summer months, becoming more variable as annual precipitation decreases. The most salient feature in terms of this study is the present-day excess of potential evapotranspiration over precipitation annually over the whole region, the annual moisture deficit increasing along a gradient from north east to south west.

Annual average precipitation is about 45 cm, and evaporation varies between 81 to 86 cm (Swanson *et al.* 1988), a theoretical maximum which serves to illustrate the current annual effective moisture deficit of the area. Annual temperatures average 4°C, although this conceals much seasonal variation, ranging from January monthly mean temperatures of -13°C to 21°C in July (Swanson *et al.* 1988). The average number of days above freezing point is only 120 (Winter *et al.* 1984), and lakes are ice-covered from 3-4 months a year (usually December to March; Bright 1968). Evapotranspiration losses of surface waters follow mean temperature trends, which results in rapid concentration of salts in many lakes from April to September where groundwater exchanges do not dominate the water balance.

2.3.3 Spiritwood Lake

Spiritwood Lake (figure 2.3) in eastern Stutsman County is a deep lake lying within a glacial meltwater channel more or less obstructed by glaciofluvial sediments deposited about 10,000 years ago (Winters 1963, Timms 1992). Chemically, Spiritwood Lake would be classed as subsaline (Williams 1981) or oligosaline (Cowardin *et al.* 1979), total dissolved solids varying between about 1.5-2 g/l at present (Sauer 1988) and specific conductivity about 2750 µS/cm (Swanson *et al.* 1988). It is the deepest lake (maximum depth 16 metres) in North Dakota capable of supporting a sport fishery (Sauer 1987) and is dimictic, stratifying thermally and often chemically in both summer and winter. The lake is about 1.5 miles long and about 0.5 mile wide, and has a topographic surface catchment area of 14,900 acres of which about 9,500 acres directly contributes to the lake (Sauer 1987).

Since the mid-1970s the lake has been characterised by increasingly severe eutrophication. Blooms of mostly blue-green algae in summer reducing the recreational use of the lake and affected its fishing. The decline in water quality has been linked to increasing nutrient levels, particularly of nitrogen and phosphorous. From 1980 Spiritwood Lake has been the focus of a State management scheme to reduce levels of nutrients in the lake by pumping hypolimnetic

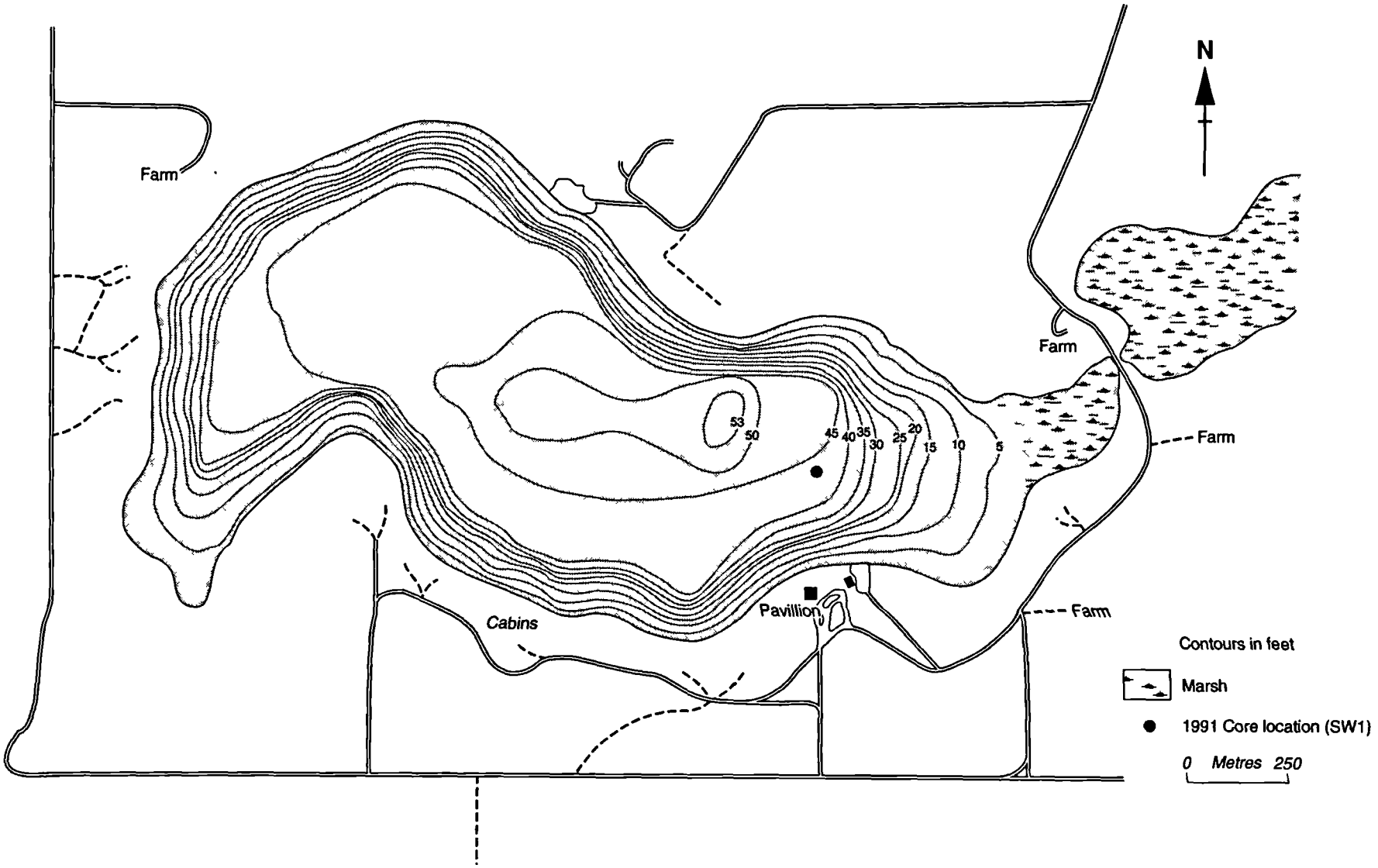


Fig. 2.3 Spiritwood Lake, Stutsman County, North Dakota

water in certain summers (Sauer 1987, 1988 & pers. comm.).

Spiritwood Lake was sampled for live diatom material during two successive field seasons, in 1991 and 1992, as part of the wider sampling programme (Chapter 3). Two short cores of about 80 cm of lake sediment were taken for sedimentary and diatom analysis in August 1991. One core (SW1) was used to test a salinity transfer function based on the weighted averaging method (Chapter 7).

Chapter 3
Methodology

3.1 Introduction

The experimental design was based on the sequential dissolution of the most frequent fresh and pristine diatom valves from the 55 lake NGP dataset (listed in Fritz *et al.* 1993). Frequency was assessed by ranking all the taxa in terms of the sum of their percentage occurrence in the surface sediment counts, from data manipulated using the PARADOX relational database. After screening the data to exclude any taxon that had not been recorded from at least one site at over 2% frequency, 120 taxa were included. The overall frequency for each taxon in the dataset was estimated by summing the percentage abundance from all sites in which it occurred. Table 3.1 lists the 60 most frequent taxa in descending order within the dataset, the most likely live habitat and for each the three sites with the highest frequency of occurrence, based on the surface sediment samples.

The choice of method for ranking the importance of taxa in the dataset is to some extent arbitrary, and one of several ways of ordering the species. As far as the accuracy of the transfer function is concerned, the most important species are those with well-defined, and preferably sharp optima, spread over the salinity gradient. It does not follow that an abundant species coincides with these criteria, as an abundant species may imply a wide tolerance (range of occurrence), with little inferential value as a precise environmental indicator (such as *Chaetoceros* cysts) or may reflect the salinity distribution of sampled lakes. The most frequent taxa in the NGP dataset include species which span the salinity range (table 3.1 & Chapter 2, table 2.1).

As the salinity gradient spans the range from freshwater to high salinity, it might be expected that the distribution of dissolution within the dataset is skewed to the high pH sites, where there is an *a priori* expectation of poor preservation (Krauskopf 1982). This is generally borne out by observation, particularly with shallow lakes, where mechanical breakage from turbulence or desiccation may also be a factor (Fritz *et al.* 1993, Flower 1993). Poor preservation is not confined to higher salinity or shallow lakes, and the relationship between salinity and pH or lake depth is not systematic within the dataset. Using parameters derived from a dataset of unevenly preserved assemblages to identify species important for dissolution experiments involves some circular thinking whatever approach is adopted. Absolute frequency provides a relatively easy basis for species choice, as it is logical that the taxa encountered most often must be the most important in the dataset (and specifically in the transfer function, Chapter 7) and will bear most

Table 3.1 - NGP taxa (surface sediment distribution)

No.	NGP code	Taxon	Habitat	Sampling sites (abundance order)		
				1	2	3
1	CH9997	Chaetoceros [elmorev/muelleri cysts]	Pl[1]	Hazelden	Free People	Basin
2	CY017A	Cyclotella quillensis	Pl	Bitter	E.Stump	Rabbit
3	CY003A	Cyclotella meneghiniana	Pl	Fife	Tramping	Twin
4	NI9997	Nitzschia [cf. fonticola]	E	E. Coteau	Big Quill	Deadmoose
5	ST010A	Stephanodiscus *parvus*	Pl	Humboldt	Roy	Albert
6	NA021A	Navicula cincta	P	Porter	Redberry	*Opuntia*
7	ST021A	Stephanodiscus minutulus	Pl	Devils	Round, Benson Co.	Albert
8	CY012A	Cyclotella caspia	Pl	George	Basin	Waldsea
9	CM023A	Cymbella pusilla	E, L	E. Devils	Medicine	Isobel
10	NI043A	Nitzschia inconspicua	E	Eckelson	W. Stump	Porter
11	AM001D	Amphora ovalis var. affinis	E, L	Long	Mission Bay	Twin
12	AU003A	Aulacoseira granulata	Pl	Herman	Spiritwood	Poinsett
13	CP001A	Campylodiscus clypeus	P	Shinbone	Horseshoe	Tramping
14	CO001A	Cocconeis placentula	E, L	Coon	Alkaline	Spiritwood
15	ST006A	Stephanodiscus niagarae	Pl	Herman	Poinsett	Madison
16	CC001A	Cyclostephanus dubius	Pl	Round, Benson Co.	Roslyn Pond	E. Coteau
17	FR006B	Fragilaria brevistriata var. inflata	Pl, Ps	Lenore	Fishing	Herman
18	FR009B	Fragilaria capucina var. mesolepta	Pl	Poinsett	Shinbone	Long
19	AN005A	Anomoeoneis costata	P	Shinbone	Alkaline	Isabel
20	NI007A	Nitzschia hungarica	P	West Stump	Stink, Stutsman Co.	Hazelden
21	RC001A	Rhoicosphenia curvata	E, L	Moon	East Devils	Alkali

[1] Habitat is coded: Pl - plankton; E - epiphyton; L - epilithon; P - epipelon; Ps - epipsammon

Table 3.1 (contd.) - NGP taxa (surface sediment distribution)

No.	NGP code	Taxon	Habitat	Sampling sites (abundance order)		
22	SU011A	Surirella peisonis	P	Fife	Shinbone	Alkaline
23	NA024A	Navicula oblonga	P	Isabel	Elbow	Fishing
24	NI014A	Nitzschia amphibia	E, L	Twin	Elbow	Long
25	NA066B	Navicula capitata var. hungarica	P	Fife	Opuntia	Fishing
26	SY005A	Synedra fasciculata	PI	Moon	Stink, Benson Co.	Coldwater
27	CO001C	Cocconeis placentula var. lineata	E, L	Long	Moon	Coldwater
28	CO005A	Cocconeis pediculus	E, L	Sayer	Deadmoose	Waldsea
29	SU002C	Surirella ovata var. crumena	P	Reflex	Tramping	Coldwater
30	NA066A	Navicula capitata	P	Norden	Madison	Long
31	NI006A	Nitzschia frustulum	E, L	Alkaline	Twin	Coon
32	FR008A	Fragilaria crotonensis	PI	Roy	Lenore	---
33	SY008A	Synedra pulchella	PI	Waubay	Alkaline	Waldsea
34	NA054A	Navicula veneta	P	Stink, Stutsman Co.	Alkali	Boucher
35	FR007A	Fragilaria vaucheriae	PI	Round, McHenry Co.	Twin	Coldwater
36	GM001A	Gomphonels olivaceum	E, L	Round, McHenry Co.	Coldwater	Fife
37	AM006A	Amphora coffeaeformis	E, L	Medicine	Waldsea	East Devils
38	DT004B	Diatoma tenue var. *elongatum*	PI	Wakaw	Fishing	Basin
39	ST001A	Stephanodiscus hantzschii	PI	Roslyn Pond	Humboldt	Herman
40	RH001A	Rhopalodia gibba	E, L	Spring	Shinbone	Moon
41	FR006A	Fragilaria brevistriata	PI	Lenore	Oakwood	Big Quill
42	AU002A	Aulacoseira ambigua	PI	Albert	Oakwood	Poinsett
43	NA9991	Navicula [cf. cryptocephala]	P	Elbow	Coon	Spring
44	NA022A	Navicula halophila	L, P	Sayer	Round, McHenry Co.	Elbow

Table 3.1 (contd.) - NGP taxa (surface sediment distribution)

No.	NGP code	Taxon	Habitat	Sampling sites (abundance order)		
45	MA002B	Mastogloia elliptica var. dansei	E, L, P	George	Isabel	Elbow
46	MA001B	Mastogloia smithii var. lacustris	E, L, P	Elbow	Lenore	Reflex
47	AM001B	Amphora ovalis var. pediculus	E, L	Norden	East Devils	Redberry
48	OP9998	Opephora (cf. olsenii)	E	Reflex	Moon	Alkali
49	CO006A	Cocconeis diminuta	Ps	Horseshoe	Fishing	Wakaw
50	NA007A	Navicula cryptocephala	P	Twin	Coon	Spring
51	GO036A	Gomphonema dichotomum	E, L	Wakaw	Lenore	Fishing
52	NI009A	Nitzschia palea	E, L	Roslyn Pond	Twin	Madison
53	SU008A	Surirella striatula	P	Waubay	Alkali	Shinbone
54	AM004A	Amphora veneta	E, L	Reflex	Stink, Stutsman Co.	Coldwater
55	CO001B	Cocconeis placentula var. euglypta	E, L	Medicine	Reflex	Waubay
56	SU002A	Surirella ovata	P	Herman	Alkali	Norden
57	NA027A	Navicula viridula	L, P	Redberry	Alkali	Fife
58	FR002C	Fragilaria construens var. venter	Pl	Herman	Roy	Reflex
59	NA056A	Navicula cuspidata	L, P	Round, McHenry Co.	Long	Spiritwood
60	AC013A	Achnanthes minutissima	E, L	Round, McHenry Co.	Wakaw	Spiritwood

relevance to the regional diatom flora generally.

Differential dissolution over the salinity gradient will tend to distort the apparent response of diatoms to salinity, depending on the robustness and the actual range of species involved. For example, robust species spanning a range of the dissolution gradient will tend to be over-represented in a mixed death assemblage as dissolution rate increases, shifting the optimum and increasing the tolerance. Conversely, fragile species may exhibit a truncated response as dissolution rate increases, altering optimum and reducing tolerance.

No sample is unaffected by dissolution, so to some extent these distortions affect all taxa, but it is the differential distribution of dissolution among taxa and sites that is a potential source of error in environmental reconstruction. The most serious problems concern those fragile taxa whose distributions owe more to dissolution processes than to response to environmental gradients. Samples which are subject to significant dissolution will be over-represented by robust forms and under-represented by fragile types, leading to over- and underestimation respectively of absolute abundance in the dataset. In a dataset of dissolved samples the most abundant taxa may be the more robust, while those fragile saline taxa with lower frequencies may be most numerous in a dataset of perfectly preserved death assemblages.

3.2 Sampling strategy

3.2.1 Site and habitat selection

Samples of as many species as feasible were collected from the eighty most abundant in the dataset (table 3.1). Species were chosen on several grounds, with emphasis placed on the more abundant taxa, the more saline taxa and on the collection of as many representative morphological types as possible to cover the range of dissolution sensitivity. The choice of taxa was to some extent modified by the sites that could be visited, and the seasonality of fieldwork, but a second field season was designed to fill gaps in the collections in 1991 to be sampled in 1992. Samples were also provided from two UK sites for three taxa, which could not be adequately sampled in the NGP. As far as possible, all experimental material was taken from lakes within the NGP.

Diatoms were sampled from epilithic, epipsammic, epipelic, epiphytic and planktonic habitats depending on the range of habitat available at each site and the species concerned (table 3.2 & 3.3). Initially, three sites were chosen for each species where it had been recorded in greatest proportions in surface sediment samples, from data held at the Limnological Research Center (LRC) in Minneapolis. While such samples were imperfectly preserved to some degree and

Table 3.2 - Sampling programme (1991)

No.	Lake	Date (1991)	Epiphyton	Epilithon	Epipelon	Epipsammon	Plankton
3	Basin	9/8				✓	✓
6	Big Quill	8/8			✓		✓
9	Coon	4/8	✓				
10	Deadmoose	9/8	✓		✓		
11	Devils	4/8		✓		✓	✓
14	East Devils	4/8	✓	✓		✓	
15	Elbow	5/8	✓			✓	
17	Fishing	8/8		✓		✓	
18	Free People	5/8					✓
22	Horseshoe	5/8	✓	✓		✓	
23	Humboldt	8/8	✓				✓
25	Lenore	9/8		✓		✓	✓
37	Rabbit	9/8				✓	✓
38	Redberry	11/8				✓	
41	Round, Benson Co.	11/8	✓		✓		
44	Sayer	9/8					✓
47	Spiritwood	3/8	✓	✓		✓	✓
46	Spring	5/8	✓	✓		✓	✓
52	Wakaw	9/8	✓				
53	Waldsea	9/8		✓		✓	✓
55	West Stump	4/8	✓		✓		

Table 3.3 - Sampling programme (1992)

No.	Lake	Date (1992)	Epiphyton	Epilithon	Epipelon	Epipsammon	Plankton (H=Hongve)
1	Albert	21/9					✓H
2	Alkali	18/9		✓	✓		✓H
---	Alkaline I[2]	18/9	✓	✓	✓		✓
---	Alkaline II[3]	15/9	✓	✓	✓		✓
8	Coldwater	18/9					✓H
11	Devils	14/9					✓H
14	East Devils	14/9	✓	✓	✓		
---	East Stump[4]	12/9			✓		
12	Eckelson	16/9			✓		
15	Elbow	13/9		✓	✓		
19	George	16&17/9	✓	✓			✓H
20	Hazelden	19/9			✓		
21	Herman	22/9		✓		✓	✓H
22	Horseshoe	13/9	✓	✓	✓		
24	Isabel	15/9			✓		
27	Madison	22/9					✓H
28	Medicine	20/9	✓			✓	✓H
29	Mission Bay	14/9	✓				✓H
30	Moon	12/9	✓		✓		✓

[2] Conductivity : 1200 $\mu S.cm^{-1}$

[3] Conductivity : 12000 $\mu S.cm^{-1}$

[4] Conductivity : 68000 $\mu S.cm^{-1}$

Table 3.3 (contd.) - Sampling programme (1992)

No.	Lake	Date (1992)	Epiphyton	Epilithon	Epipelon	Epipsammon	Plankton (H=Hongve)
31	Norden	21/9				✓	
32	Oakwood	21/9					✓ H
35	Poinsett	22/9					✓ H
---	"Powerline"[5]	16/9			✓		
40	Roslyn Pond	19/9					✓ H
41	Round, Benson Co.	13/9		✓	✓		✓ H
43	Roy	19/9					✓ H
45	Shinbone	13/9	✓	✓	✓		
47	Spiritwood	16/9	✓	✓	✓	✓	✓ H
48	Stink, Stutsman Co.	16/9	✓		✓		
54	Waubay	20/9			✓		✓ H
55	West stump	12/9	✓		✓		

[5] Unnamed lake, very near Stink Lake (Stutsman Co.)

might not reflect contemporary conditions in the lake, this system seemed to offer the best chance for finding fresh diatoms *in situ* from a large area in a limited time. Each taxon had back up sampling sites if collections could not be made, or were not found at any given lake. Although the surface sediment relative abundance could not be taken as an accurate reading of the absolute abundance of that taxon in the lake at the time of sampling, it provided an indication of it, and implied that there were habitats in the current limnological environment that supported these species.

Sampling was not quantitative, in that standard areas of habitats were not sampled. This was not considered necessary as the object of sampling was the collection of as much material as possible for experimental dissolution.

Samples for experimental work, and microscope study, needed to be fresh, preferably living, at time of collection, in large abundance and with a high percentage of the species of interest. It was important to keep non-diatomaceous clays and mineral matter and older, reworked diatom silica at a minimum wherever possible from the perspective of both routine analysis and experimental procedure. For all these reasons, the most appropriate samples were those from living habitats rather than surface sediment samples. Generally, all habitat samples except plankton provided good diatom material, as seasonality was less important an influence on diatom standing crops. In the case of plankton samples, due to the short duration and unpredictability of bloom conditions the stocks of many planktonic forms (notably centrics) were taken from surface sediment samples.

3.2.2 Epilithon

Epilithic samples were taken from pooled samples of several adjacent large stones in the nearshore photic zone, and where possible replicated at a separate site at the lake. Stones were gently scrubbed clean with a soft filament toothbrush and rinsed several times into Sterilin tubes with lake water. Some lakes were associated with muddy stones which may represent a distinct community (Juggins 1992).

3.2.3 Epipsammon

The epipsammon consisted of those coarse to fine grained sands in nearshore areas. Previous studies (Round 1965, Hickman 1969 , Cameron 1990) have suggested this supports a distinct community which, despite large absolute abundance at least in terms of standing crop, is relatively under-represented in surface sediments offshore. Only the uppermost millimetres of the sand surface was removed. Samples were washed in lake water to remove

detrital matter not strictly part of the epipsammon.

3.2.4 Epipelon

Where the nearshore areas consisted of fine to very fine mud, epipelic samples were taken by skimming the uppermost few millimetres of the mud. Most measures to separate the diatom cells from these samples to remove the actual epipelic community (*e.g.* gradient centrifuging) were not possible in the field. They have been reported as having mixed results, none being completely effective. The only method that could be employed, the lens tissue technique (Eaton & Moss 1966) preferentially isolates motile species from the flora, which are not necessarily those taxa of interest.

3.2.5 Epiphyton

Various macrophytes were sampled for diatoms, ranging from stem scrapings from reeds, to whole submerged aquatic plants (such as *Ruppia* spp.). Representatives of all major plant types at each site were sampled including collections of filamentous algal mats.

3.2.6 Other samples

Occasionally, it was possible to take diatom scrapes from artificial structures at the lakeside and in one case from the buoy of a sediment trap (Lake George). Of these samples only the last was used in this study.

3.2.7 Plankton samples

Plankton was sampled by filtration of water collected in a Ruttner bottle at a depth of 0.5 m below the water surface away from the shore. Six litres were usually taken at one time from which one or two litres were filtered on shore using Whatman GF/F (0.45 µm) glass fibre, or cellulose nitrate filters (0.45 µm & 1 µm). A section of the filter was scanned under field microscope to determine sample suitability. Diatoms were fixed by addition of Lugols iodine prior to filtration.

In the first field season, July-August 1991, no diatom plankton blooms were found, and in most cases blue-green algae (cyanophytes) dominated the plankton, although small concentrations of living diatom cells were sometimes present. Consequently the second field season was timed to coincide with a late summer-early autumn bloom, associated with the autumn turnover after the decline of other plankton groups (Happey-Wood 1988, Sommer 1988). In several of the

lakes sampled monthly in the region no spring bloom occurred (S.C.Fritz & K. Laird, pers. comm 1992). During the second field season, in September-October 1992, several large centric species were present in high enough concentrations to filter, although only one lake was sampled during a true diatom-dominated bloom (*Chaetoceros* sp. in Coldwater Lake).

3.2.8 Surface sediment samples

Surface sediment samples were taken using a Hongve gravity corer from a boat in the 1992 field season. Two samples were taken from the deepest areas of each lake, but in different sites, below the photic zone. Sediments were subsampled in the field at 0-0.25 cm and 0.25-1 cm levels approximately, and stored in Whirlpak bags. Using a field microscope it was possible to differentiate cells at various stages after death, based on the integrity of the cell contents. Although it was not possible to estimate the time since the last bloom this did provide a means of comparing relative recency of deposition and of assessing the potential for taphonomic degradation. These samples were only used in experiments where diatom analysis showed good preservation and little non-diatomaceous material.

3.2.9 Spiritwood Lake samples

Live diatoms and sediment samples were collected on both field seasons. The living community was sampled from a variety of habitats around the lake shore (table 3.2, 3.3). Two short piston cores (78 cm & 82 cm) were taken in August 1991 from a depth of 13.4 m.

3.3 Field and laboratory techniques

3.3.1 Field preparation and storage

All live samples were treated with either Lugol's iodine or glutaraldehyde soon after collection and stored in iceboxes until refrigeration at the LRC. Samples were subsequently returned to UCL and stored at 4°C. Subsampled surface sediments were stored without pretreatment. During fieldwork on both trips, all collections were scanned with a field microscope, capable of magnification under bright field at x600. Samples were also scanned at x750 at the LRC. This was not sufficiently good for critical taxonomy but was very useful in assessing sample suitability. Generic and specific identification was possible for some samples but was hampered by organic debris, mineral matter and cell contents. The presence and appearance of cell contents was in itself a good indication and check on diatom preservation, and confirmed the lack of living cells in surface sediments.

3.3.2 Sample preparation

3.3.2.1 Introduction

Subsamples were taken from all homogenised bulk samples and treated using standard methods (Battarbee 1986, ECRC 1993) to evaluate those most appropriate for experimental work. Preparation techniques for material to be used in experiments varied for each sample type, and had to be modified to some extent from standard techniques in line with the aim of the study, and the constraints of the experimental method. Diatoms could be separated from detrital matter in some cases by the techniques of differential settling and wet sieving, taking advantage of relative and absolute size differences between sediment fractions. Plankton samples concentrated on Whatman cellulose nitrate filters, also required additional pretreatment.

In order to minimise the effect of breakage on the valves, the gentlest preparation techniques should be used. The epilithic, epipelic and epiphytic fractions can be prepared by heating in 30% H_2O_2, at 70-80°C, in large Pyrex beakers as the samples are too organic for oxidation by the standard water bath technique, which was preferentially used. The problem with the epipsammic flora is twofold; to remove the non-attached (dead or not truly epipsammic) diatoms and detritus from the sand, and to remove the attached diatoms from the fine sand grains themselves, which can be achieved by a decantation process (which was found to be as effective as filtration) before and after oxidation in a water bath at 85°C for 4-5 hours.

3.3.2.2 Differential settling

Differential settling involves suspending oxidised sample in distilled water with the addition of a few drops of Decon-90 dispersant. The solution is then agitated. The settling vessel itself is a glass separating funnel, which allows easy removal of the bottom fraction from the water column with the minimum of disturbance to the sample. This is allowed to settle for 2-6 hours before the lowest level is poured off. The sample can then be centrifuged to concentrate the solids and wash out any Decon-90.

3.3.2.3 Wet sieving

Where necessary, oxidised samples were wet sieved with 20 µm and 38 µm nylon mesh. In all such cases, sediments were pre-filtered at 180 µm to remove the coarsest mineral matter and organic debris before subsequent filtration. To aid flocculation of clays and other particulates, samples were pre-treated by adding a few drops of Decon-90 just before all sieving. The

residue (or filtrate) can be centrifuged to concentrate solids and wash out any Decon-90.

3.3.2.4 Treatment of cellulose nitrate filters

Acetone was added to those samples collected on Whatman cellulose nitrate filters as a filter solvent. To avoid using excessively large volumes of acetone, these were treated as normal samples and oxidised with 30% H_2O_2 cold for several days and then hot (up to 85°C) for 1-2 hours to dislodge diatoms from the filters. The filters and supernatant were scanned at x400, showing that this process was effective. All matter remaining in the filters was strongly enmeshed within the filter and could only be removed by solvents. As the largest filter pore size used was 1 µm, this material consisted mainly of mineral fragments and clay particles.

The filters were removed from the solutions when they appeared white to the eye. There was some disintegration of the filters during oxidisation, but this could be removed by addition of acetone to the sample in glass test tubes and immediate centrifuging (4 minutes at 1200 rpm), repeating after replacing the supernatant with distilled water. This extracted almost all the filter left in the sample without the risk of evaporation of acetone leading to precipitation of cellulose nitrate from the solution.

3.3.2.5 Filtration of large diatoms

Samples from Eckelson Lake and Shinbone Lake scanned at x1000 revealed large numbers of *Anomoeoneis costata* (Eckelson), *Campylodiscus clypeus* (Shinbone) and *Surirella peisonis* and *Surirella ovalis* (Shinbone). The largest particles in the sediment were these diatoms, and although there was much diatomaceous material of a much finer size (the bulk of which appeared detrital - that is, consisting largely of badly dissolved and broken fragments of old sedimented valves), only the well preserved, larger taxa were of interest.

Removal of mineral matter, detrital diatom silica and clays serves four purposes:

1. Removal of non relevant, and in this case smaller, taxa;

2. Removal of detrital silica, potentially more easily soluble (Lewin 1961), to try to keep to the principles of the experiment, namely, dissolution of fresh (recent) diatoms;

3. Removal of fine clays and mineral matter, to ease in subsequent counting under LM, SEM and inverted microscope;

4. Reduction in the surface area of clay minerals, which may act as sites for preferential redeposition of dissolved silica, even below saturation levels in the supernatant (Flower 1993 & pers. comm.).

A means of separating the finer material from the larger fractions would therefore greatly improve the purity of the material, in terms of both the species composition and general sediment characteristics of the sample. The dissolution rate of the sample would more closely reflect the silica loss from the species of interest, rather than being influenced by the other sediment fractions. A variety of approaches were considered to address the problem, including differential settling in water and methanol, flotation techniques in heavy liquids, and wet filtration using soil sieves.

Differential settling cannot be relied upon on to remove all the finer fractions even after repetition of the process, although for the larger diatoms in a clay matrix, this method might be very effective. Dense liquids, such as sodium tungstate or zinc chloride are expensive, although they can be re-used, and may involve unnecessary exposure to harmful chemicals. Wet sieving was tested first as an efficient, fast, clean method for cleaning such samples.

The technique was used for separating diatom valves from several samples, and depending on the valve size concentrated on the filter mesh or in the filtrate.

3.3.3 Experimental Pretreatment

All samples for dissolution experiments must be pre-treated identically as far as possible to justify the assumption that differences in dissolution behaviour are not the result of experimental variability. To this end, all samples for all experiments were treated with H_2O_2 for approximately the same length of time at the same temperature (85°C).

Recent results have implicated diatom preparation techniques as a significant source of sample preservation problems, especially vigorous treatments involving hot peroxide solutions and concentrated HCl treatment (pers. comm. Flower & McKay). As several recommended preparation techniques involve these procedures (for example, Battarbee 1986) this is an area of some concern for diatom analysis, particularly for samples initially at different taphonomic stages. Care was taken to try to minimise sample damage during preparation and while it was recognised that excessive temperatures and specifically the use of HCl could and should be avoided, observations on both fresh and sediment samples suggested no discernible difference between the preservational state of assemblages before and after treatment with hot (but not boiling) H_2O_2. A degree of sample cleaning was necessary, and the method adopted was based

on a compromise between ease of laboratory operation, material and equipment availability, and time available for this aspect of the work against the apparent quality of the prepared samples.

The only aspect of the pretreatment that could be damaging is the use of hot hydrogen peroxide, but personal repeated observations (of a range of valve robustness and initial preservational condition) on the material used for these experiments and core samples suggested that the most practical approach was pragmatic; there might be little improvement in sample quality for much expended time and effort. As other workers have used similar methods without adverse comment, it was decided to keep the preparation methods as gentle as possible, chemically and physically, whereby several small steps to remove the most hazardous aspects of treatments could be made easily, to the point where further improvements seemed only possible at much greater effort.

3.3.4 Diatom analysis

Diatoms were identified and counted using both Nikon and a Wild research quality microscopes at magnifications of x1000 and x750 respectively, under phase contrast illumination. Scanning electron microscopy (SEM) was also used for taxonomic and morphological analysis on Hitachi microscopes on several machines with gold sputter-coated samples (Golden 1989). Micrographs were taken under light microscopy on black and white 35 mm film (100 ASA), and on both Polaroid and Tri-X Pan (400 ASA) under SEM. Abundance measurements during the final dissolution experiments were made using an inverted microscope under bright field at x1000 and customised settling chambers.

Live samples were counted to 300 valves or over in initial screening, and for preliminary experimental work. All samples counted during final experimental work were counted to at least 400 valves, except where too few valves made this impractical. All diatom abundances were estimated using the microsphere method of Battarbee & Kneen (1982). Estimates for 0.95 confidence limits were assigned to percentage and abundance data where appropriate, using Mosimann's equations for the binomial approximation to the normal distribution, as given in Maher (1972) and Birks & Gordon (1985).

Standard floras were consulted for taxonomic identification, including Hustedt (1930-1966, 1955, 1957), Krammer & Lange-Bertalot (1986-1992), Archibald (1983), Germain (1982) and Patrick & Reimer (1966, 1975), as well as various occasional publications and papers in journals such as *Diatom Research*, *Journal of Paleolimnology* and *Hydrobiologia*.

3.3.5 Data presentation & analysis

The live and surface sediment sampling strategy involved the identification of many taxa not included in the most abundant taxa as recorded in the 55 lake dataset, from a diversity of habitats and lake water chemistries. Only the most frequent taxa (table 3.1) were used in dissolution experiments (Chapters 4 and 5).

Some counts were made using a PC keyboard set up under the programs POLCOUNT (Maher 1992) and COUNTER (Hamilton 1990). Applications to transfer functions involved the programs TWINSPAN (Hill 1979), CANOCO 3.12 (ter Braak 1988, 1990) and CALIBRATE v.4 (Juggins & ter Braak 1993). All numerical analyses were performed on an IBM PC compatible.

3.3.6 Dissolved silica analysis

During dissolution experiments, supernatant dissolved silica levels were analysed according to the method in Golterman *et al.* (1978). Silica will form a yellow complex with molybdate ions (MoO_4^{2-}) between pH 3 and 4 which is reduced with tin (II) chloride ($SnCl_2$) to a blue complex. Absorbance is measured at 815 nm and obeys Beer's law between 0.1-5.0 mg/l SiO_2-Si. Eight standards were used for all determinations and checked regularly throughout the analyses for spectrophotometer drift. Analyses were made on spectrophotometers in the Departments of Biology and Geology, UCL.

3.3.7 Physical & chemical analysis of Spiritwood short cores

Cores were extruded in the field at 1 cm intervals to 30 cm and in 2 cm slices to the base. Loss on ignition (LOI) and percentage carbonate content (CO_3^{2-}) were calculated in the laboratory at UCL for core SW1. For each level, LOI was determined by measuring the weight loss after a known amount of dry sediment was heated to 550°C in a muffle furnace for 2 hours, and carbonate content from the subsequent weight loss on heating further to 950°C for 2 hours (Dean 1974). Samples were placed in a desiccator after each process prior to weighing at room temperature.

Chapter 4
Diatom dissolution: experimental design

4.1 Aims

Experimental design is dictated by the aims, which seek to investigate dissolution in the natural lake environment as far as is practicable. In particular, conditions of dissolution had to be found in which a diatom assemblage dissolved completely, but slowly enough so as to allow regular monitoring of the condition of the frustules and the supernatant silica concentration. Preliminary experiments were carried out on a test assemblage of diatoms to develop an experimental methodology for controlled dissolution of the American material. Development of a complete methodology involves considering technical, practical and analytical aspects. The purpose of preliminary experiments was to manipulate the factors affecting silica solubility kinetics to give an appropriate rate of frustule dissolution, within the framework of an acceptable day-to-day experimental procedure, and to consider the nature of data generated, including how best to collect, analyze and present them.

The present experimental work aims to dissolve fresh diatom frustules in a series of artificial but representative assemblages comprising the most abundant species in the NGP data set over a suitable period (several weeks) for monitoring the entire sequence of dissolution. The change in the abundance, proportion and morphology of the diatoms can be followed at regular stages in the dissolution process and related to each other. For each taxon, the dissolution sequence will be broken down into 2 or more distinct stages (where possible), identified by parallel SEM and LM micrography to enable each stage of each taxon to be consistently recognised. Using microspheres added as a spike (Battarbee & Kneen 1982), abundance changes for individual species and samples can be related to changes in valve morphology and percentage composition of the assemblage.

Taxa which are widespread (such as *Cyclotella* species) can be used as indices of dissolution for the entire sample, as long as the relationship between the rate of dissolution between taxa is fairly constant, which can be tested by repeat experiments. These indicator taxa will reduce the need for counting each taxon separately to arrive at a dissolution value for the sample (which is envisaged as a weighting for species populations and so proportions in the sample). Barker (1990, 1992) calculated the ratio of total to dissolved *Cyclotella meneghiniana* (those which lost their marginal areolae), and used this to provide an index of preservation for comparing differently dissolved samples.

The dissolution indices should in themselves be useful in improving the qualitative inferences that can be made about the actual death assemblage and so the diatom community and lake environment that supported it. Incongruous taxa, or samples, those for which the dissolution index appears as an outlier in dissolution behaviour, may underline taphonomic problems of sediment mixing (from whatever cause) as valves deposited at the same time should follow the same paths of relative dissolution. This may be obvious from the ecological preferences of the taxa involved, but provides an independent means of showing this, based on physico-chemical processes alone, and may be useful if the ecological information is less black-and-white.

Experimental results can be applied to a salinity transfer function from the NGP dataset in the form of sample and species weighting based on dissolution rank. The Spiritwood core has an independent role as a study of environmental change in the last 150 years and will be used to explore the palaeolimnological value of dissolution indices and ranks, both in qualitative interpretations of environmental change and quantitatively in environmental reconstruction involving transfer functions.

4.2 Past and present experiments

4.2.1 Theoretical aspects of silica dissolution

The rate of dissolution of solid silica can be described in terms of the difference between concentration of the solution and its saturation value and the specific surface area of the solid, as follows (Hurd 1972):

$$\frac{dC_{sol}}{dt} = k_2.(C_{sat} - C_{sol}).S \qquad (1)$$

where:

$\delta c_{sol}/dt$ is the rate of silica dissolution per unit time, in moles.cm^{-3}.sec^{-1};
k_2 is the rate constant in cm.sec^{-1};
C_{sat} and C_{sol} the value of the saturated and unsaturated solutions respectively, both in moles.cm^{-3};
S is the surface area of the available solid per unit volume of solution, in cm^2.cm^{-3}, or cm^{-1}.

It is only since the 1950s that accurate and reliable values for C_{sat} at low temperatures have been found for different forms of silica (Krauskopf 1956 / k Iler 1979). Conflicting results were produced from

early experiments due to the very slow kinetic rates of dissolution and precipitation of solid silica, and the confusion caused by complex reactions between solid, dissolved and colloidal forms of silica. There is still uncertainty over the hydrated state of silica, to the extent that it remains unclear which dissolved species of silica are detected by colo rimetric analyses (*e.g.* Golterman, Clymo & Ohnstad 1978). Marshall & Warakomski (1980) found distilled water saturated at 25°C between 2290µm (137.4mg/l) and 2100µm (126mg/l) SiO_2, or 64.1mg/l and 58.8mg/l Si respectively, which compares well with other values and other forms of synthetic and biogenic silica in the literature. Krauskopf (1956) quotes the values of Alexander *et al.* (1954) for amorphous silica at 25°C, from pH between 0-9, of 100-140 ppm SiO_2, which is about 47-65mg/l Si, and Lewin (1961) found her solutions saturated at around 45mg/l Si at pH 9 and 19°C.

If detailed, and accurate, information on the specific surface area and the dissolved silica concentration was available for these experiments, it would be possible to estimate values for the rate constant and, by integration, predict when saturation, or rather complete dissolution for these assemblages, would occur. Dissolution experiments can provide estimates of $\mathbf{k_2}$ for experiments, if assumptions about **S** are made (typically 50-150 m^2/g for fresh siliceous phytoplankton, Lawson *et al.* 1978) and if dissolved silica (values of **C**) can be reliably measured. This would allow some comparison with published research on the dissolution rates of naturally decomposing, acid-cleaned biogenic silica, and amorphous synthetic gels (*e.g.* Hurd 1972, Lawson *et al.* 1978, Hurd & Theyer 1975).

Equation **(1)** is extremely useful conceptually in explaining some of the difficulties inherent in any study concerned with silica dissolution rates. The rate of dissolution among the solutions should increase with the saturation concentration ($\mathbf{C_{sat}}$), which should affect both the proportions and abundance of valves, and the time of disappearance of species in the assemblage in each solution, although it should not affect the ranking, if a stable rank relationship exists amongst species in the assemblage.

The value of $\mathbf{k_2}$ will depend on the experimental conditions, ionic strength, temperature and pH of the solution, and pretreatment of the assemblage, which can be controlled in an experiment to a large extent. The greatest discrepancy between, and within, experiments is changes in the value of **S**. Different assemblages will have different initial specific surface areas, and more importantly they will change during the course of an experiment, as the proportion of species in the assemblage, and the condition of individual valves within species, alters. Variation in $\mathbf{k_2}$ and **S** (measured for diatom valves by liquid nitrogen adsorption, Lawson *et al.* 1978) is the most likely explanation for the much slower dissolution rate observed in many biogenic silica experiments than that of Marshall & Warakomski (1980), for example. They found that

amorphous silica gel reached equilibrium concentration within 18 hours for a range of salt solutions over about 0.5m, whereas the unsaturated salt solutions used in the first preliminary experiment (see below) failed to dissolve all silica after 14 days.

4.2.2 Experimental dissolution of diatoms

Previous experimental work has demonstrated the extent of amorphous silica dissolution in a variety of solutions, dependant on several physico-chemical characteristics, particularly the pH, temperature, salt concentration and composition. While the exact extent of dissolution under any given set of parameters can be predicted from empirically-derived models to a good approximation for amorphous silica, the rate of silica dissolution is open to far more uncertainty, as the range of factors influencing dissolution rate concern mechanisms of reaction kinetics and are therefore greatly influenced by surface characteristics of the silica mass as well as the external conditions of the dissolving medium. The rate of silica dissolution, which is the ultimate concern of these experiments, is determined not only by variables extrinsic but also intrinsic to the silica solid, that is on its specific surface area, and the exact nature of the surfaces.

As far as the dissolution of biogenic diatom silica is concerned, the most important properties of the ultrastructure of frustules are the specific surface area and the condition of the silica surfaces, which is related to the cleaning process used in pretreatment of valves. Under the same conditions of dissolving medium, there is ample scope for dramatic differences in the rate, if not the final solubility of silica between amorphous biogenic and synthetic silica[1], as well as between identical biogenic samples pretreated differently. Add to this the differences in external experimental conditions between different researchers and the difficulty in trying to dissolve diatom samples at a predetermined, controlled rate in the absence of a complete silica dissolution model is considerable.

Standardisation of dissolution experiments is almost impossible logistically and undesirable methodologically as each experiment is designed within its own framework to satisfy individual aims. In the case of biogenic silica solubility, there are too few experimental observations cited to quantify all the variables involved, and there are still uncertainties involved which only empirical experiment can resolve.

Although a wide variety of essentially laboratory-based dissolution experiments have been carried out on diatoms, as well as other siliceous and non-siliceous organisms such as foraminifera, since the 1950s at least (eg Jorgensen 1955a), there has been relatively little from a specifically

[1]Amorphous silica gel has been shown to have a lower absolute solubility and dissolution rate in the presence of Al ions (Iler 1973, cited in van Bennekom 1981)

quantitative, palaeoecological perspective. Experimental dissolution work has been carried out on calcareous microfossils in a marine context (*e.g.* Berger 1970, Hill 1975, McIntyre & McIntyre 1971, Metzler *et al.* 1982). High temperature annealing has been used to simulate the fossilization process for radiolaria (Afanasieva 1990).

The table (4.1) shows some examples of the range and nature of previous work on the dissolution of biogenic silica, although there are several more in the scientific literature on amorphous and crystalline silica solubility (and precipitation) in general which are applicable to the problem. Only that of Parker *et al.* (1977) is carried out in the actual lake environment, but even here the lake water has been filtered and the dissolution assemblage pretreated in the laboratory by ashing the organic fraction. Diatom dissolution rates may be increased by natural bacterial populations in lakes, which may be associated with the production of hydolitic enzymes which decompose an outer organic layer retarding dissolution (Patrick & Holding 1985).

The first consideration is in the treatment of diatoms themselves from collection to experimentation (Chapter 3; Flower 1993). Biogenic samples should be treated carefully after collection to minimise any changes to the frustule from the living state. According to results of pretreatments in previous work (table 4.1) dissolution of valves is increased by removal of the organic coating of the diatom, but there is evidence of metal ions associated with the frustule surfaces which slow the rate of dissolution down to a much greater degree (although Mayer *et al.* (1991) found that diatom dissolution was enhanced in the presence of high concentrations of iron oxides). This layer can be removed rapidly by acid cleaning in particular. Hydrochloric acid is often added to remove carbonates and stop oxidation by hydrogen peroxide, but cannot be used here. Samples can be effectively cleaned with hydrogen peroxide alone for SEM and LM work.

Temperature control during pretreatment is important as biogenic silica can undergo changes which may affect its solubility. Lewin (1961) found that frustules heated to "redness" in a crucible were less soluble, when compared with samples dried at room temperature and those kept "wet", with all other experimental conditions kept constant, while Marshall (1980a) showed that amorphous silica gel dried at 110°C had a slower rate of dissolution at 25°C than if it was dried at room temperature. Amorphous silica may undergo some crystallization at these higher temperatures, affecting the equilibrium solubility, while lower temperatures may reduce the specific surface area, and lower the rate of dissolution.

Experiments were also carried out using a centrifuge to see at what speed damage occurred to the valves, and what was the best combination of time and speed to settle diatoms. The

Selected previous experiments on biogenic silica[1]

Reference	Materials	Pretreatments	Main solvents	Mol	pH	Temp (°C)	Time	Notes
Jorgensen (1955b)	cultured diatoms	methyl killed	HCl	?	5	?	2-6d, 6-85d	Dissolution varied @ taxa
			$KHCO_3$ K_2CO_3		8 & 10			
Krauskopf (1956)	diatomite	none	artificial seawater	?	?	85-95	20d[2]	Low dissolution
Lewin (1961)	cultured diatoms, plankton, diatomite	various[3]	TRIS buffer (+/- seawater)	0.01	9 (3-9)	19 (6-35)	40-50d (10-110d)	Dissolution @ pH, temp, age & pretreatment
Kamatani (1971)	cultured diatoms, plankton, diatomite, sponge spicules	acid wash, drying at 110°C	NaCl Na_2SO_4 $MgCl_2$ $CaCl_2$	0.34 0.14 0.21 0.18	7	100	1h	Dissolution varied @ taxa, age, salt (pH) & temperature
			Na_2CO_3	0.19	10	100	1h	
		none	Na_2CO_3 & H_2SO_4	~0.2	1.5	100	2h	
		acid wash	seawater	Cl=½	?	15-20	24d	
		none	seawater	Cl=½	?	100	2h	

[1]Where figures are given in brackets, these refer to the range of values used in various experiments. Time refers to the total experimental duration, as follows: **m** = months, **w** = weeks, **d** = days & **h** = hours.

[2]Bottle leaked after 20 days

[3]Live cells were killed with heat, protein-denaturing agents, organic solvents, and breakage. Pretreatments of dead cells included washing in nitric acid (and experiments carried out on both dried and non-dried material), and treating with DHEG, EDTA (and/or oxalate) and solutions of metal ions. Experiments were also carried out on untreated, *live* cells.

Reference	Materials	Pretreatments	Main solvents	Mol	pH	Temp (°C)	Time	Notes
Hurd (1972)	biogenic opal >62µm	HCl wash, drying at 100°C	seawater	?	?	3	~19h	Stirring increased dissolution rate
						25	~4h	
Johnson (1974)	Quaternary diatoms, radiolaria & sponge spicules >62µm	H_2O_2 & HCl wash; ultrasonic cleaning; dried at 110°C	Filtered, natural seawater	?	?	?	10-500h	Differential dissolution; index derived
Hurd & Theyer (1975)	radiolaria/sponge spicules (40My-Recent age)	acid wash	seawater	?	8.3	3 & 25	3-6m	Stirred; dissolution @ age
Bailey-Watts (1976)	fresh planktonic diatoms	Some killed at 40°C for 15 mins	Filtered loch water or deionised water	?	?	4, 10 & 20	38d-15.5m	Greater dissolution from initially living cells & higher temperatures
Kastner *et al.* (1977)	cultured & Quaternary diatoms	low temperature oxygen plasma ashing	filtered seawater	?	8	room temp	1-3w	Dissolution @ age; seawater better solvent
			distilled H_2O	n/a	7			
Mikkelsen (1977)	Pliocene diatoms	10% HCl & 10% H_2O_2; clays separated by sieving & settling	natural seawater	6µM SiO_2	8.1	25	200h	Shaken; differential dissolution; some amorphous silica overgrowth
Parker *et al.* (1977)	fresh diatom frustules	ashed at 500°C	filtered lake water	?	?	c.4	27d	10-12% SiO_2 dissolved by end
Lawson *et al.* (1978)	fresh plankton	none	filtered seawater	3.3% sal.	7.9-8.2	7-28	10d-20d	Aerated & stirred. Slow dissolution

Reference	Materials	Pretreatments	Main solvents	Mol	pH	Temp (°C)	Time	Notes
Mikkelsen (1980)	Pliocene diatoms, radiolaria & silico-flagellates	10% HCl 10% H_2O_2	filtered seawater	?	8.1	25	650h	Shaker bath. Assemblage composition changed
van Bennekom (1981)	fresh plankton	freeze dried & low temperature ashing; dried at 105°C	filtered surface ocean water	?	8.1	12	5500h	Shaker used. Dissolution @ Al content of frustules
Glover (1982)	fresh and sedimented diatoms	living, UV killed & "cleaned"	lake water	?	<9	5 & 20	230d	Dissolution related to temperature & pretreatment
Erez *et al.* (1982)	fresh radiolaria (*Castanidium longispinum*) & sponge spicules	none; bleached with 5% NaOCl for 25 mins at room temp	seawater *in situ*	?	?	?	61d	Maximum dissolution at subsurface; radiolaria dissolve faster than diatoms
Rippey (1983)	Lough Neagh sediment (top 20cms)	none	lake water & borate buffer	?	7.4-9.0	3-25	30d	Biogenic source for dissolved SiO_2, @ temperature & pH
Kamatani *et al.* (1988)	marine surface diatomaceous ooze	none or acid washed (HCl or HNO_3 + H_2O_2) at 100°C & 5°C; dried at 50°C	filtered seawater	3.3 % sal.; 20µM SiO_2	7.9	25	1.25-603h	Acid treatment increased dissolution rate; specific surface area decreased over time

Reference	Materials	Pretreatments	Main solvents	Mol	pH	Temp (°C)	Time	Notes
Shemesh *et al.* (1989)	Diatoms of Holocene, LGM & ^{18}O isotope stage 5e age	none	Na_2CO_3	2	12	60 & 85	1-4h	Dissolution @ temperature & age
van Bennekom *et al.* (1989)	deep-sea fan surface sediments & fresh plankton	freeze dried & low *temperature* ashing	filtered natural seawater	?	7.8-7.9	12	1 year	Dissolution reduced by Al
Barker (1990)	Pleistocene diatoms	various (none, HCl & H_2O_2)	Na_2CO_3	2	12	60 & 85	1-4h	Dissolution @ temperature & pretreatment
Mayer *et al.* (1991)	cultured marine diatoms (*Odontella aurita*)	organic layer removed by pronase & heating to 400°C for 1 hour	seawater; iron ferrihydrite added (up to 300 mg-Fe/g-sediment)	?	?	room temperature	2-7w	Iron oxides increased dissolution rate; dissolution stages developed
Pichon *et al.* (1992)	diatoms & silicoflagellates from marine surface sediments	"dried and moderately crushed"	Na_2CO_3	2	12	60	120h	Samples agitated; differential dissolution; transfer function developed
Flower (1993)	fresh to Miocene (6-8 Myr BP) diatomaceous sediments from saline & freshwaters	various (none, acid & H_2O_2 cleaned at 90°C & room temperature; centrifuged or not)	Na_2CO_3; $MgCO_3$; $CaCO_3$; distilled water	various	various	room temperature - 50	up to 12d	Dissolution & breakage related to pretreatments, pH, temperature; differential dissolution & stages identified

Reference	Materials	Pretreatments	Main solvents	Mol	pH	Temp (°C)	Time	Notes
Barker *et al.* (1994)	freshwater plankton, diatomaceous surface sediments & quartz	sediments dried & disaggregated; fresh cells enzymatically cleaned	various salt solutions (chlorides, carbonates & nitrates) & distilled water	0.6 M-3 M	4-11.3	*room* temperature	46d-92d	Dissolution greatest at high pH; differential dissolution; dissolution stages identified

relationship between speed (rpm) and centrifugal force is not linear, but varies in proportion to the square of the angular velocity for a given mass and radius of rotation. Centrifugal forces in liquid/solid suspensions are also affected by relative densities and frictional forces between liquids and solids. Low speeds can be used for longer periods below the threshold of breakage, which varies for different species, and is important to establish to save time in initial preparation of samples (to reduce breakage influencing the dissolution experiment), and when a sample is analyzed during the experiment to get valves representative of the stage of dissolution for LM and SEM work at the time of sampling. These tests have only used fresh frustules, and as it is hypothesised that frustules will be more easily broken as they corrode, further work could be done on dissolved material to establish how the centrifuge speed must be reduced to minimise "non-experimental" breakage. No difference was observed between identical prepared samples centrifuged 4 times at 1200 rpm for 4 minutes and those settled under gravity overnight, which was subsequently the procedure adopted for processing samples.

4.2.3 Test assemblage

All preliminary experiments were carried out on an identical assemblage of diatoms, made up by mixing 4 live samples collected from fresh and subsaline lakes in Argentina. These samples were in large supply, and microscope analysis confirmed the purity and quality of the material after (identical) pretreatment, as outlined in Chapter 3. This assemblage included taxa which covered a range of species size and morphology within a relatively small species diversity, and provided good overlap with the American material.

4.2.4 Sample mixing

Evaluating the relative dissolution behaviour of many taxa necessitates dissolving them together, which involves finding a compromise between two experimental methods. Very few of the NGP samples as collected in the field contained taxa of interest in sufficient abundance, or proportion that they could be used as complete dissolution assemblages in themselves. Sample mixing was inevitable to some degree as each dissolution assemblage had to include common species to allow correlation between different species along one scale of dissolution ranking. At the other extreme, samples including all species of interest could not simply be added together to form one experimental mixture, as then most species would make up a very small proportion of the whole, necessitating very large count sums to enable accurate percentage changes to be followed. Logistically, it was not feasible to run experiments in an unlimited number of containers, as there were constraints on both laboratory equipment and processing time involved in monitoring each mixture. Using several different samples mixed together in different proportions, depending on species composition and abundance, to create

a series of dissolution assemblages provided the compromise between these extreme situations.

In order to work out the mixing ratio of samples, a matrix was set up using simple mixing ratios, assuming in the first case, that each sample had the same diatom concentration. This can be formalised as follows:

$$\sum_{x=1}^{p} \alpha_x i_x \sim 100 \qquad (2)$$

where:

α is the variable weighting factor for each sample **x** (of **p**) to be mixed, such that $0 \leq \alpha \leq 1$, and $\Sigma\alpha_x = 1$;

i_x is the percentage of species **i** in sample **x**, for all species encountered in all samples.

There are of course any number of possible combinations of the various factors, but it is possible to define what the ideal combination would be, and so the "best" assemblage. For example, the test assemblage is designed to cover the spread of species resistance, this is one which maximises the number of species thought highly likely to differ in their susceptibility to dissolution, in suitable proportions (those which could be followed with some statistical assurance at whatever count level is employed). There is already some *a priori* reasoning in deciding which species will differ in their susceptibility, which is based on their absolute dimensions and apparent silica thickness as viewed under LM, but this may not be an accurate guide to specific surface area (Lawson *et al.* 1978) or frustule ultrastructure. The total count sum chosen will affect the lower limit of proportions which can be followed with statistical confidence, and must be balanced against the time involved, which is a subjective assessment. Again, these are considerations which these preliminary experiments can investigate, if not resolve absolutely.

By a process of trial and error, a combination of mixing factors can be found which gives a good species combination in each final assemblage. These factors can then be adjusted according to the concentration of diatoms in each sample, to judge the weight needed of each constituent sample suspension. Most samples had high concentrations of diatoms per gramme so that in the prepared suspensions the danger of diluting the dissolving solution is avoided. All weights were measured on an electronic open-top balance accurate to 4 decimal places.

An example of this process of sample mixing is shown in the table 4.2. The mixing factors, applied to the matrix of samples, can be altered to find the "ideal" assemblage, from which the weights of each component sample needed can be calculated, based on the concentration of valves in each sample and the total number required in the dissolution experiment that the assemblage represents.

4.2.5 Initial diatom concentrations

Six subsamples containing different numbers of valves from each assemblage were placed in plastic test tubes and dissolved in 0.2 M NaOH at 85°C in a water bath (following Krausse *et al.* 1983), and the dissolved silica concentrations analysed according to Golterman *et al.* (1978; Chapter 3). Final diatom concentrations (estimated using microspheres added to subsamples of final assemblages, Battarbee & Kneen 1982) were chosen which would not saturate experimental solutions (pH10, 25°C).

4.2.6 Initial assemblage composition and counting strategy

Figure 4.1 shows the 0.95 confidence envelope that can be expected for the proportions of the taxa observed as count sum increases four fold using Mosimann's equations (see Chapter 3). Although there is only a minor improvement in confidence limits as the sum is increased, this is disproportionately important for low percentages. As the count is increased from 100, to 400 and 1000 valves, the margins of error are reduced, but are still relatively large at low values (around 5%), and asymmetric, tending to favour underestimation at the lower end of the scale. Counting errors decrease as the square root of the count sum, but count time increases linearly, a feature that has been analysed by Maher (1972) in a discussion of the optimum count size. Again, this will depend on the point of the count, and the scale and accuracy of trends that suit the analyst. The maximum number of species that could be followed in an assemblage is a compromise between the asymmetrical relationship between statistical accuracy and counting time spent on each sample. By choosing mixtures of samples in which each of 5 or 6 species of interest made up 5-15% or more of the initial assemblage a count sum of 400 valves could be employed as an optimum strategy taking advantage of the control over initial species composition in sample selection.

4.3 Preliminary experiments

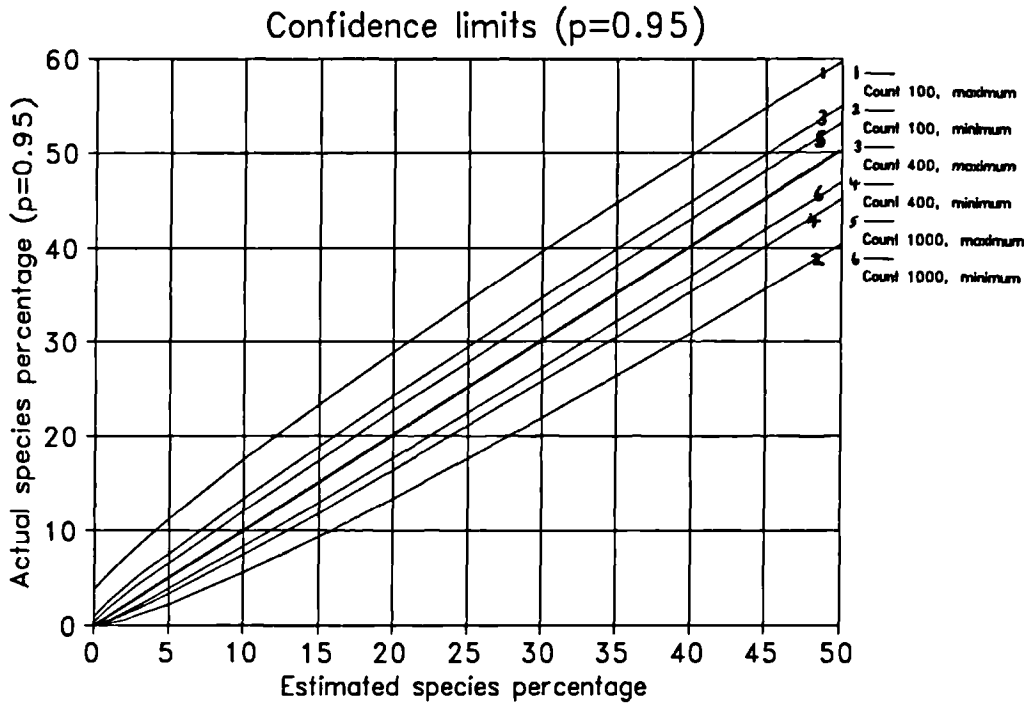
4.3.1 Dissolution in salt solutions

Salt solutions were chosen to cover a range of dissolution rate as the solubility of a polar

Table 4.2 An example of Mixing Ratios

	Sample: AG3	AG5	AG12	AG14	Totals	Control
Mixing Ratios	**0.25**	**0.25**	**0.2**	**0.3**	**1**	**t=0**
Achnanthes minutissima	7.1				7.1	5.5
Cyclostephanos tholioformis		3.8		2.7	6.5	6.5
Cyclotella meneghiniana		1.8			1.8	1.2
Fragilaria vaucheriae		9.3	3.1	14.0	26.3	30.5
Gomphonema olivaceum				7.1	7.1	8.8
Aulacoseira granulata var ang						
Aulacoseira varians			7.6		7.6	5.0
Navicula cincta		1.2			1.2	
Navicula veneta			3.5		3.5	4.5
Navicula (AG5)			1.8		1.8	
Nitzschia palea		5.2	2.9		8.1	12.2
Nitzschia frustulum	0.8	2.2	2.6	5.2	10.8	8.2
Nitzschia gracilis			1.0		1.0	
Synedra acus	10.8				10.8	9.6
Amphora veneta	n/a	n/a	n/a	n/a	n/a	3.7
Totals	18.66	23.43	22.50	28.88	93.46	95.70

Figure 4.1 - Counting confidence limits



species decreases as ionic strength of the solvent increases, although dissolved silica is theoretically less prone to this effect as undissociated silicic acid, H_4SiO_4 (Krauskopf 1982). Silica solubility decreases with increasing electrolyte concentration, especially at low temperatures (c.25°C), and is least soluble of all in solutions of salts with high hydration numbers, which relates to the valency of the metal ion (Marshall 1980a, 1980b, Marshall & Warakomski 1980, Fournier & Marshall 1983). Sodium and magnesium salt solutions are therefore likely to be most effective silica solvents at low concentrations, and sodium salts more effective than those of magnesium at all concentrations. This has been demonstrated for their sulphates on experiments with amorphous silica gel at 25°C (Marshall & Warakomski 1980) over the pH range 4-9, where saturation silica concentrations only decline slightly with increasing sodium sulphate concentration up to salt saturation.

The first exploratory dissolution experiments were carried out on the test assemblage using solutions of the two salts dominating lake water chemistry in the NGP, mirabilite ($Na_2SO_4.10H_2O$) and epsomite ($MgSO_4.7H_2O$). Eight solutions at various ionic strengths and composition were made up in stoppered polyethylene flasks and an equal amount of identical test assemblage was added to each. Microspheres were also added to monitor diatom abundance decline. Flasks were kept under cover at room temperature and agitated by shaking twice a day.

Each day, a measured volume of well-shaken solution was withdrawn using an Eppendorf pipette, and the valves washed and concentrated by low speed centrifuging. The supernatant after the first spin was decanted with a Pasteur pipette and refrigerated for subsequent silica analysis (see Chapter 3). Permanent slides for LM and SEM analysis were prepared from the washed residue, and the remainder suspended in methanol and refrigerated in glass phials.

4.3.2 Results and discussion

Dissolving diatoms in salt solutions proved to be unsuitable as an experimental method in this situation, although other researchers have employed the technique. At room temperatures, the rate of silica dissolution was too slow, despite reported potential dissolved silica saturation levels (between about 1320µM and 1970µM SiO_2 at 25°C, Marshall & Warakomski 1980) that were well above initial solid silica content. Barker *et al.* (1994) found that equilibrium values of dissolved silica from diatom valves and quartz in salt solutions up to 3 M at room temperatures were not in agreement with theoretical model predictions, and were well below these for 5 out of 7 solutions.

Additionally, there were several practical problems associated with salt solutions. Abundance

counts were unreliable and it was subsequently discovered that the material the microspheres were made of, 95% polystyrene and 5% divinyl benzene, had a density of around 1.05 g/cm^3, while that of the salt solutions ranged from 1.06-1.2 g/cm^3. Microspheres were preferentially pipetted off after each rinse, which prevented any diatom abundance change to be linked to proportional variations.

Absolute salt content, even at low molalities, was such that it took over 5 washes in the centrifuge to ensure a sufficiently good slide quality for counting, which added considerable time to the daily procedure. Marshall & Warakomski (1980) found that the yellow colorimetric reaction to determine silica concentration using the ammonium molybdate complex was delayed with solutions containing magnesium salts, with the full colour only developing after up to 8 days. The technique for silica analysis used here (Golterman, Clymo & Ohnstad 1978) involves reducing this yellow complex with tin(II) chloride and analysing the blue compound. It was found by silica standard addition to magnesium and sodium sulphate solutions that the appearance of the blue colour was delayed in the presence of magnesium sulphate.

4.3.3 Diatom dissolution as a function of pH

Given the problems experienced with salt solutions, a second preliminary experiment was set up using buffered pH solutions to dissolve the test assemblage. Silica solubility, which is effectively independent of pH below pH9, rises exponentially above pH9 (Krauskopf 1956, 1982), in which category most of the NGP dataset falls (Chapter 2). The high pH of these lakes is likely to dominate silica dissolution at these temperatures and salinities. For comparison, the pH of the salt solutions, although not controlled, was in the range of 4-7 in all cases over the course of the previous experiment.

4.3.4 Method

Three 250ml solutions of different buffered pH were made up in 500ml high-density polyethylene flasks, using laboratory-distilled water and Whatman borate buffers, nominally pH7, pH9 and pH10. Initial pH values measured with a digital pH meter were pH7, 9.36 and 10 respectively but were all well-buffered and measured within 0.1 units of their initial values throughout the experiment. Although the densities of the buffers were measured at between 1.01 and 1.02 g/cm^3, it was decided to add microspheres after the final wash given previous problems. In this way, the proportion could be adjusted in line with diatom decline nearer the optimum ratio.

Equal amounts of the test dissolution mixture, identical to that added to each salt solution, were

added to each flask of buffer (250g distilled water). To reduce the inherent variability in ambient laboratory temperature, the flasks were kept in a dark incubated water-bath shaker set at 25°C (chosen as a standard temperature used in much of the literature, and in keeping with potential real lake temperatures). The shaker also allowed constant gentle, orbital mixing of the samples, instead of twice-daily shaking of the salt solutions. These differences between the experiments are minor compared with changes in the dissolution rate that can be expected at these higher pHs.

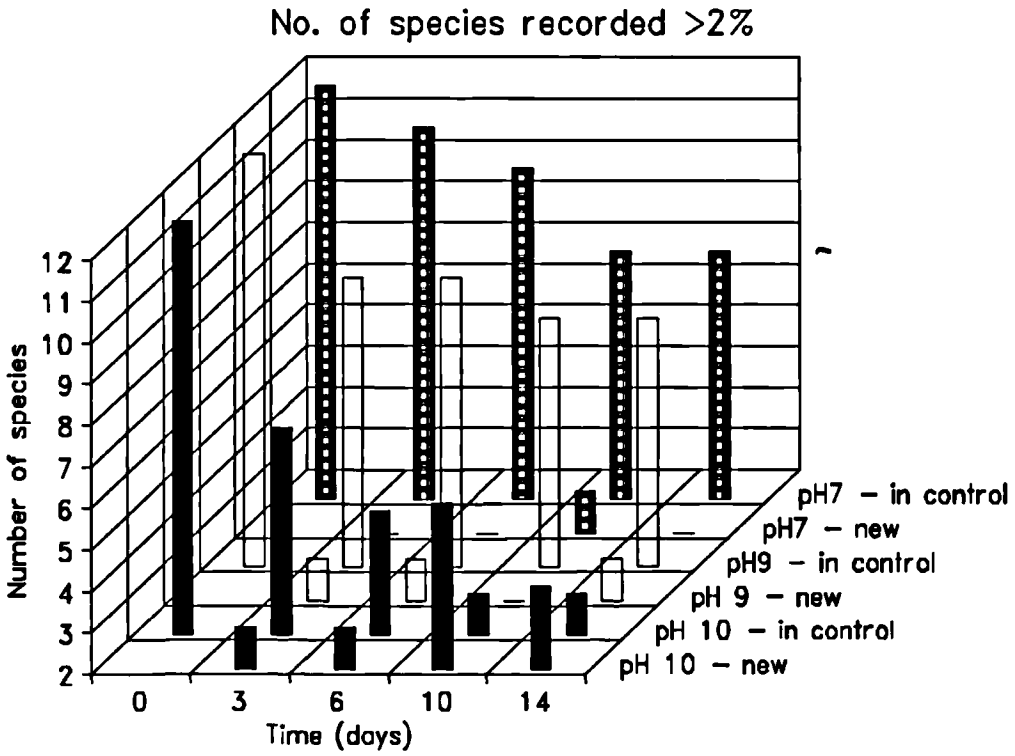
Samples were taken at 4 times over a fortnight to check the progress of dissolution on days 3, 6, 10 and 14, and compared in each case with the count to 600 made of the assemblage originally and used as the control in the salt experiments. A weighed amount of microspheres was added to each sample after washing. Two or three washes with distilled water were sufficient to give good slides and from each sample two coverslips were prepared by drying overnight. Dissolution was to all intents and purposes stopped after two washes as there was no appreciable buffer left. Counts of 300 valves were made using both coverslips mounted in Naphrax. In two cases (days 10 and 14 at pH10) diatoms were in such small numbers on the coverslips that only 200 and 150 valves respectively were counted after several hours. The number of microspheres encountered was used to estimate the absolute abundance change, as a count outside the sum.

4.3.5 Results

Differences between assemblages at different pH were much greater than those found between different salt solutions, as there was much larger variation in the dissolution rate between solutions. Differences in the robustness of taxa were clearly expressed in the percentage counts over the 14 days, especially at high pH. At all pH's, the dominant taxa was *Fragilaria vaucheriae*, but its importance declined over the 14 days at high pH where distinctions in the robustness of taxa were clearly expressed in the percentage counts, particularly for the *Cymbella* taxa. The *Nitzschia* and centric species present were preferentially dissolved and the more silicified and often rarer forms, such as large *Cymbella* species, became increasingly important in the assemblage.

Figure 4.2 summarises differences in dissolution behaviour at each pH over the experiment, by comparing the number of species identified from each sample over 2%, compared to the initial (control). The figure also shows the appearance of taxa not encountered in the initial count (invariably robust taxa), despite a much greater count sum of 600 valves. There is an apparent watershed in the evolution of the assemblage at pH10, which clearly separates the buffer solutions in terms of dissolution rate.

Figure 4.2 - pH and diatom dissolution



4.4 Ranking species resistance

The species can also be ranked in order of resistance to dissolution from changes in percentage over time. Various rank ordering indices have been proposed, and subsequently used to produce indices of preservation for samples based on the weighted average of assemblages of ranked species. These compare well with other indices involving other more general microfossil and mineralogical characteristics of sediment (Berger 1968, Johnson 1974, Thunell 1976, Mikkelsen 1980, Berger *et al.* 1982) to classify a sample's preservation status. Berger (1968), for example, ranked the 15 most common species of foraminifera from a central Atlantic surface sediment data set from paired samples within 300 miles at different depths, as dissolution was essentially a depth-dependant function. For each pair, he calculated the ratio of the difference to the sum of proportions of each species, averaged across all pairs of samples at different depths, and ranked them.

To investigate the usefulness of the approach for the NGP material, species were ordered according to Mikkelsen (1980), who ranked species of marine diatom according to their changing proportions over time in a dissolution experiment. Each species was given a resistance index, r_i, as follows:

$$r_i = \frac{n_{i(t)}}{n_{i(0)}} \qquad (3)$$

where:

n_i is the proportion of species **i**, at time **t** compared to the initial proportion.

Species can be ranked in descending order of the values for the index, such that the most resistant species has the rank 1, and so on. Mikkelsen based her ranking on two replicate counts of 300 valves each, and found little change in the final ranking after the first time interval counted (250 hours). In each case for this experiment the initial time is taken as the control proportions (**t=0**).

For each sample, the resistance ratios were ranked from 1-19, tied value being given equal rank. A final ranking was made, by averaging the sum of ranks for each species at each pH and ranking this (table 4.3); this represents the average position of four trials at each pH. If a real, repeatable ranking exists between the species, it should result in a stable ordering where

Table 4.3 pH Ranking of Argentinian material

Rank pH7		Average	pH7 t=0,3	pH7 t=0,6	pH7 t=0,10	pH7 t=0,14
1	Cymbella sp	1.0	1	1	1	1
2	Cymbella cistula	2.8	3	2	4	2
3	Achnanthes minutissima	4.5	5	3	5	5
4	Navicula veneta	4.5	2	7	6	3
5	Fragilaria vaucheriae	6.8	7	6	7	7
6	Synedra acus	7.0	9	5	8	6
7	Gomphonema olivaceum	7.3	8	8	9	4
8	Navicula sp	7.8	4	10	3	14
9	Cyclotella meneghiniana	8.5	15	4	2	13
10	Nitzschia communis	9.8	6	9	15	9
11	Aulacoseira varians	11.3	12	11	11	11
12	Gomphonema sp	11.8	14	13	12	8
13	Amphora veneta	11.8	11	12	14	10
14	Nitzschia frustulum	12.3	10	14	10	15
15	Cyclostephanos tholioformis	13.3	13	15	13	12
16	Nitzschia palea	16.3	16	17	16	16
17	Nitzschia sp	16.8	17	16	17	17
18	Rhoicosphenia curvata	17.8	18	18	17	18
19	Epithemia sorex	17.8	18	18	17	18
Rank pH9		**Average**	**pH9 t=0,3**	**pH9 t=0,6**	**pH9 t=0,10**	**pH9 t=0,14**
1	Cymbella sp	1.3	2	1	1	1
2	Cymbella cistula	3.3	1	3	6	3
3	Acnanthes minutissima	4.5	6	5	3	4
4	Gomphonema sp	5.0	8	8	2	2
5	Gomponema olivaceum	5.5	4	6	4	8
6	Fragilaria vaucheriae	6.0	5	7	7	5
7	Navicula veneta	7.5	12	4	8	6
8	Navicula sp	8.0	16	2	5	9
9	Cyclotella meneghiniana	8.5	3	13	11	7
10	Aulacoseira varians	10.3	7	11	9	14
11	Synedra acus	10.3	9	9	10	13
12	Nitzschia frustulum	11.8	13	10	14	10
13	Cyclostephanos tholioformis	13.3	10	14	13	16
14	Nitzschia sp	13.3	11	15	15	12
15	Nitzschia communis	13.8	15	11	15	14
16	Amphora veneta	14.5	17	18	12	11
17	Nitzschia palea	16.3	14	17	17	17
18	Epithemia sorex	17.5	18	16	18	18
19	Rhoicosphenia curvata	18.5	19	19	18	18
Rank pH10		**Average**	**pH10 t=0,3**	**pH10 t=0,6**	**pH10 t=0,10**	**pH10 t=0,14**
1	Cymbella cistula	1.5	1	2	2	1
2	Cymbella sp	2.8	7	1	1	2
3	Cyclotella meneghiniana	4.3	2	9	3	3
4	Gomphonema sp	5.0	5	3	4	8
5	Fragilaria vaucheriae	5.5	4	5	7	6
6	Gomphonema olivaceum	6.3	6	7	8	4
7	Rhoicosphenia curvata	8.3	17	4	5	7
8	Navicula veneta	8.5	8	6	10	10
9	Synedra acus	8.8	9	8	9	9
10	Achnanthes minutissima	9.8	3	11	13	12
11	Aulacoseira varians	9.8	14	1	12	12
12	Epithemia sorex	10.0	17	12	6	5
13	Navicula sp	11.8	10	10	15	12
14	Nitzschia frustulum	12.3	11	13	14	11
15	Amphora veneta	13.0	12	17	11	12
16	Cyclostephanos tholioformis	14.3	15	15	15	12
17	Nitzschia communis	14.3	13	17	15	12
18	Nitzschia palea	14.8	16	16	15	12
19	Nitzschia sp	15.3	17	17	15	12

sufficient dissolution has occurred to be able to differentiate species robustness. It may be expected that the rankings within each pH converge together as time (and so total dissolution) progresses, and that this convergence occurs sooner as pH increases from 7 to 10.

The order of species in the final rank (the order of the taxa in the table) differs between each pH solution in detail, although agreeing in general. In all three solutions, the *Cymbella* species are the top two ranking taxa, although it is only at pH10 that *Cymbella cistula* is ranked first. The greatest differences between the rankings split pH7 and pH9 from pH10, corroborating the different percentage and ratio changes at high pH, as dissolution rate increases exponentially. *Achnanthes minutissima* has an average rank of 4.5 at both pH7 and 9, and is ranked third overall in both cases, while at pH10, this more than doubles to 9.8 and gives a final ranking of equal 10th.

The table points to several differences in the rankings at different pHs, in part due to the method of ranking itself. Species that disappear completely are assigned the same rank in the present system, which can lead to misleading final rankings as these positions are tied. This is only noticeable at pH10, and artificially lowers the rank where several taxa disappear. One possible solution within this ranking system is to assign the same high rank to all species.

If dissolution rate is the only difference between the pH-buffered solutions, it might be expected that the evolution of the assemblage follows the same path at each pH, but reaches different stages at any given time, depending on the rate. At 25°C, the solubility of silica is about 120ppm SiO_2 at pH7, 150ppm at pH9 and about 350ppm at pH10 (Krauskopf 1982), which if translated directly into a dissolution rate (all other conditions being equal) implies an increase of 300% over the pH range of these buffers.

Dissolution has occurred in all situations, and as there is no reason to suspect from theoretical considerations or empirical evidence that the *nature* of dissolution is any different in any solvent, it is fair to assume that the processes have been the same. Differences in the results accordingly stem from different kinetic rates of dissolution.

4.5 Abundance of valves

At first sight, the technique of adding microspheres after sample washing and counting proportions to diatoms on the same slides used for LM analysis appeared to have been completely successful. The data for pH 9 and 10 suggested a log-linear decay relationship, with only 2-3% of original diatom numbers left after 14 days at pH10:

$$\text{pH9: } \text{Ln(pop.\%)}=4.374-0.0707T_d \quad n=5,\ r^2=0.609 \qquad (4)$$

$$\text{pH10: } \text{Ln(pop.\%)}=4.572-0.2860T_d \quad n=5,\ r^2=0.988 \qquad (5)$$

Where T_d is the experimental time in days

The shallower fall in abundance at pH9 than pH10 is as predicted from the increase in the dissolution rate, and in both instances outstrips percentage increases in species observed. For all taxa there is population loss, but at a rate depending on the robustness of each.

4.6 Sample processing

4.6.1 Preparation losses

Subsequently, it was discovered that another problem, more subtle than the previous density complication, was affecting the microsphere count and introducing bias to the results. It was suspected that the diatom decline was too steep, implying preferential loss of diatoms during subsample processing. A further series of experiments was set up to evaluate the seriousness of this error.

Correctly employed, the microsphere method has been demonstrated to be a reliable, accurate and relatively easy means for estimating diatom abundance (Battarbee & Kneen, 1982), and can be legitimately and justifiably used in preference to other labour intensive counting strategies. Generally, microspheres are added to final suspensions of diatoms and settled at room temperatures overnight onto coverslips for counting under LM. Values for diatom abundance will then relate to the number at this stage of preparation, and do not take into account any losses of valves that may have occurred during processing. These amounts are generally considered negligible (relative to sample size) and in any case a systematic error common to all samples.

In the case of these dissolution experiments, processing losses may not be so unimportant. Firstly, because of the limited supply of experimental diatoms, and the need to prevent silica saturation in the solutions, the number of valves in each flask and the corresponding number removed per subsample are relatively small. This was not thought to pose any particular problems. No references could be found concerning diatom losses during preparation in the literature and only through personal correspondence was the problem mentioned (Simms 1993, Peabody 1993, pers. comm.).

4.6.2 Diatom losses from centrifuging

An experiment was set up to compare the effects of centrifuging, method of microsphere addition, and test tube type, on diatom and microsphere numbers. A measured weight of prepared diatom suspension, of likely subsample size, from the NGP material, was added to several centrifuge tubes of polystyrene (A-C) or glass (I-III) and the volume made up to 10mls with distilled water. The diatom abundance per gramme was checked by adding a known number of microspheres to one sample and settling out a slide overnight and counting under LM, and agreed with the previous determination of concentration for the sample. These results add internal consistency to the microsphere method. Silica content analysis of several samples enumerated using microspheres agree with the range of values published in the literature and provides independent evidence that supports Battarbee & Kneen's conclusion that the microsphere method can be used to give a good estimate of the actual numbers of diatoms in a sample.

Samples A and I are controls, and were not centrifuged. Samples B, C, II and III were centrifuged according to standard methods (ECRC 1993), four times at 1200rpm for four minutes, each time removing the supernatant with a Pasteur pipette, and then refilling the test tube with distilled water to 10mls. Microspheres were added to the samples either before (B and II) or after (C and III) centrifuging and two slides for each sample made up at the same time, settled overnight at room temperature. Microspheres were added gravimetrically to all samples accurate to 4 figures. All slides were counted for diatom/microsphere ratios to at least 300 valves under LM at x1000, and each observation represents the average of two counts. For each pair of values, the larger figure was within 10% of the smaller.

The results of this experiment are shown graphically in the following two figures (figures 4.3 & 4.4). The process of centrifuging and supernatant removal appears to cause a loss of diatoms *and* microspheres, but proportionally more microspheres are lost (test tubes II & III, corresponding to B & C). The loss of diatoms and microspheres is reduced in glass test tubes (test tube III, compared to C; test tube II, compared to B).

This experiment is not an exhaustive study of all the possibilities, but a qualitative initial investigation of 6 variables of preparation technique (centrifuged before, after or not at all before microsphere addition; glass or plastic test tubes). Interpreted in this way, the following table (table 4.4) illustrates the relative losses of diatoms and microspheres during the washing process (centrifuging and supernatant removal):

Figure 4.3

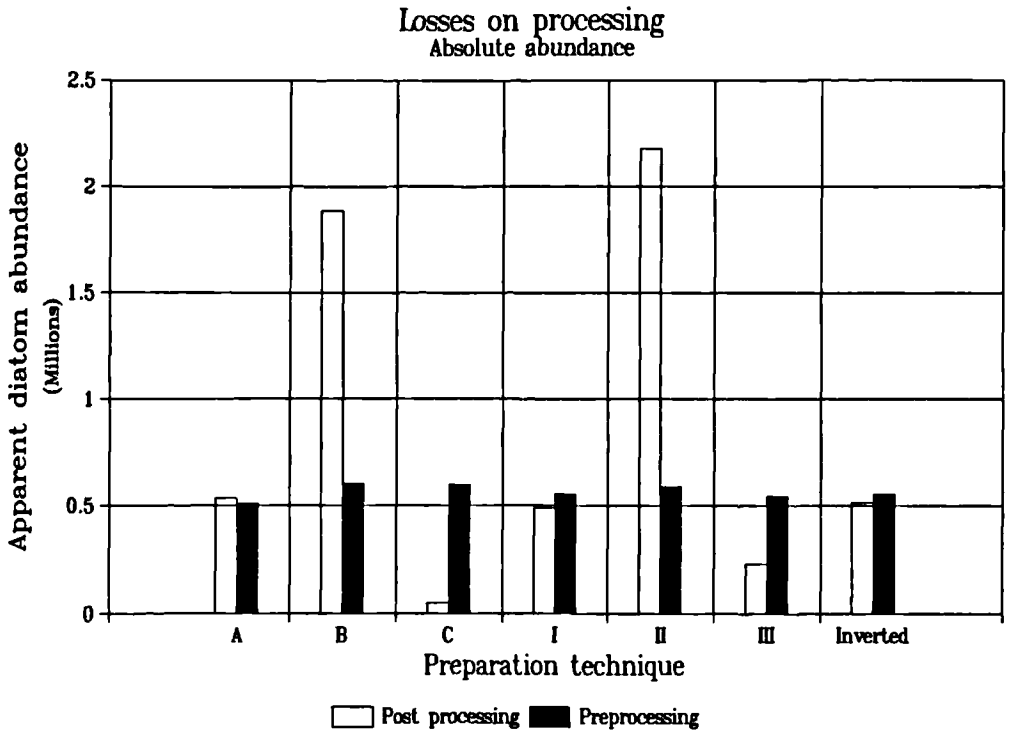


Figure 4.4

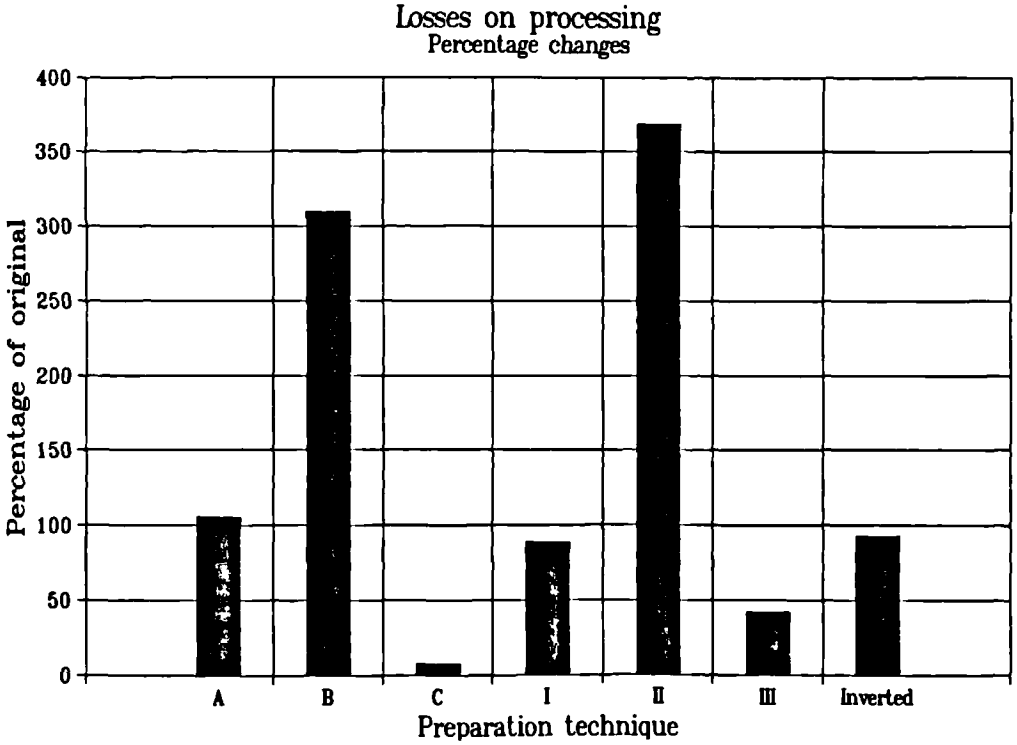


Table 4.4 : Preparation losses

Proportion left	Glass test tube	Plastic test tube
Diatoms	0.42	0.08
Microspheres	0.11	0.03

Diatoms and microspheres may be bound to the surfaces of test tubes, or pipettes, a phenomenon which has been noted by diatom analysts before (Simms 1993, Peabody 1993, pers. comm.). The strength of this attachment may be strong at the surface of the test tube, and this initial layer may cause further material to be caught and prevented from sedimenting to the bottom of the test tube. During supernatant removal, it was observed that material was dislodged as the water level fell in the test tube, some of which was unavoidably removed with the supernatant. As supernatant could not be withdrawn without this effect, loss of material seemed inevitable. It was not possible to explore the situation further in this research, and these suggestions are offered as hypotheses requiring investigation. Reducing surface tension in the wash might reduce the force on the test tube sides as the fluid level fell, and lessen the amount of material dislodged into the supernatant. Sites of attachment on the sides of the test tubes might be preferentially occupied by added ions.

A small series of qualitative observations investigating these points was made. Identical samples to those used in the centrifuging loss experiment were spun in glass test tubes with various washes. Methanol (ρ=0.793g/cm^3) mixed with distilled water was compared with samples spun in solutions containing large numbers of ions by adding drops of Decon-90 and dilute NH_4^+ to distilled water. Results suggested no discernible improvement with ionic solutions, but less dislodgement with a methanol-water mix, and more material appeared to be sedimented to the bottom of the test tube. This could be due to the lower density of the methanol mix, reducing the impedance to friction and so increasing actual settling force slightly. Additionally, ions attaching to clay particles in the suspension may have reduced their settling rate substantially. On the basis of these observations, it was decided to wash samples the minimum number of times, in glass test tubes using a methanol-distilled water mixture.

4.6.3 Discussion

Diatom losses during processing are probably not considered important as sample size for routine analysis, even in techniques such as the water bath method (Renberg 1990), involve many millions of valves. The losses reported here are in the order of perhaps hundreds of

thousands or less over 4 washes, and may depend more on the area inside test tubes and the number of washes. This figure is unlikely to have a significant effect on numbers for these large samples, as losses are not proportional to sample size above some critical threshold. In these experiments, sample sizes cannot be as large as in conventional work, and so the only other option is to minimise the significance of losses by maximising sample size, as far as possible.

In order to minimise this effect, minor changes were made in the experimental design. Glass test tubes were used for centrifuging, and samples should be washed the minimum number of times, as supernatant removal appeared to be the process most associated with losses. The only major change in experimental design was the inclusion of a separate process to monitor abundance changes, as washing altered the microsphere/diatom ratios unpredictably. This was incorporated using a Leitz inverted microscope under bright field at x1000, on samples containing microspheres settled directly from the dissolution flasks into wells designed for the purpose. Each well volume was 2.26 cm^3 (1.2 cm deep, radius 0.775 cm). A calibrated volume of 50% HCl added to samples immediately after withdrawal from the flasks neutralised the buffer solution, and prevented further dissolution during settling time. The density of the neutralised solution remained below that of the microspheres, and tests showed that samples settled well within the 4 hours allowed, including 15 minutes for CO_2 outgassing from the solution. There were a few problems in some samples where gas bubbles developed about the same size as microspheres, perhaps due to temperature changes, but these could be resettled if identification proved a problem.

Replicate counts (to 300 valves) confirmed that this was a reliable means of estimating diatom/microsphere ratios, comparing closely with samples prepared for LM study (sample A, I and "Inverted" in figures 4.3 & 4.4). The use of the inverted microscope counting method is described in more detail by Lund, Kipling & LeCren (1958). The low refractive index of solutions did not present difficulties in differentiating valves from other material, but was not sufficiently good for unambiguous taxonomic identification.

This system also had the advantage that there was a much shorter time lag between taking a sample and evaluating the abundance change, without waiting overnight for LM slide preparation. Nearer real-time monitoring of dissolution behaviour enables sampling strategy to match the progress of dissolution, particularly in the early stages of logarithmic population decline.

Diatom abundance change as observed in the pH experiment is partly an artifact of the method, and overestimates the rate of diatom loss. These results give an indication that diatom losses through experimental technique are an important source of error in abundance estimation,

potentially swamping the signal from dissolution. Although the actual abundance changes at pH10 cannot be confidently estimated, systematic processing errors are superimposed on a significant diatom decline, supported on theoretical grounds, and by changes in individual valve morphology and assemblage composition. The conditions of pH and temperature should remain as the rate of dissolution is of the right order, and more time should be allowed for the experiment. If the population decline is monitored interactively, the rate can be regulated as necessary.

4.7 Final experimental design

The final experimental design was developed as a result of the experiences of these preliminary experiments, but was also refined in small ways during the course of both major experiments, as large, multiple samples taken involved different aspects of scale. These changes were details, and in essence the most important aspects of the method were decided on the results of these earlier experiments. Dissolution was carried out in high-density polyethylene, stoppered flasks, in a covered water bath shaker at 25°C, in distilled water buffered at pH10. Six assemblages were used in the first, and five in the second experiment, to which were added a quantity of microspheres such that the initial microsphere/diatom ration was about 0.25, about half the optimum value recommended by Maher (1981) but which would increase as diatoms dissolved. A small amount of mercury(II) chloride ($HgCl_2$) was added to each flask to inhibit bacterial or other growth (Patrick & Holding 1985), and the experiment sampled regularly as the assemblage dissolved.

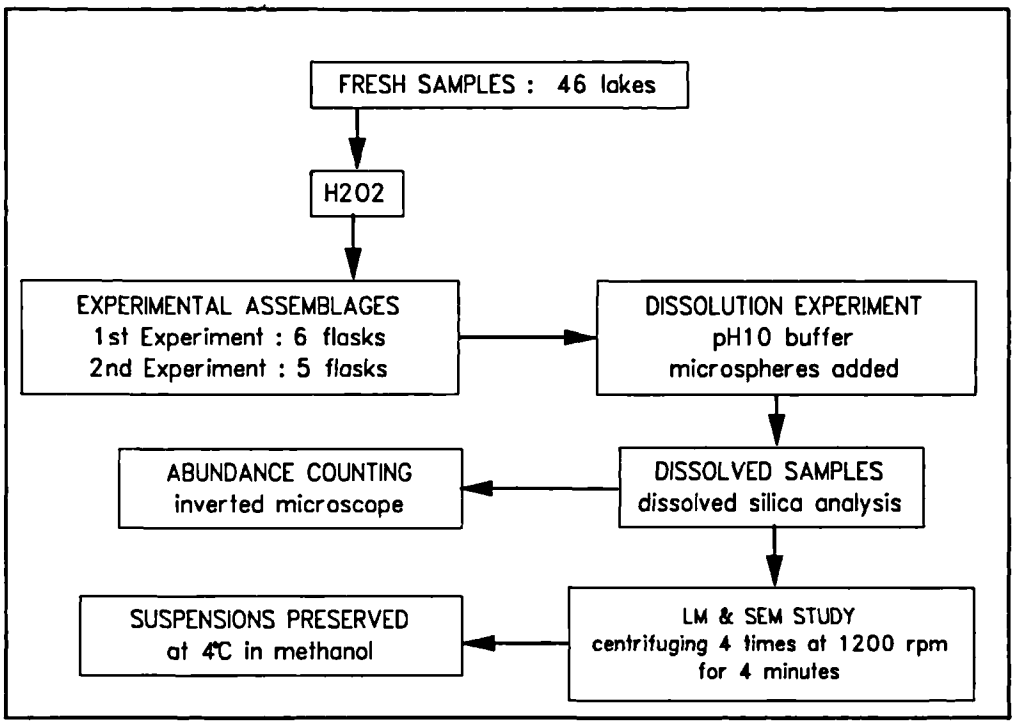
This experimental design from sample pretreatment to final processing and analysis is summarised in the diagram below (figure 4.5).

4.8 Experimental Problems

4.8.1 Experimental design

Not all taxa in the NGP list could be covered in either experiment because they were not present in large enough numbers in the field collections, and similarly, some species not specifically targeted, were included in dissolution experiments due to abundance in several samples and for comparison. Non-coverage in the dissolution experiments may be partly solved by comparing morphologically similar species which are covered. Correlation between assemblages and experiments was achieved by including common taxa from the same samples collected in 1991 to all flasks.

Figure 4.5 - Experimental design



These experiments are entirely laboratory-based in conditions of controlled environment, and although the detail and particularly kinetics of dissolution are unrealistic of North American lakes the basic processes and so outcome should be the same (a fundamental assumption). The logistical impossibility of experimenting on, and monitoring, a representative sample of the most abundant in the field, with so many other factors uncontrolled, from water chemistry (major ions to trace elements), temperature, pH and other known and unknown influences is in itself justification for laboratory work, at least as an initial step. In many ways, there are distinct advantages in the laboratory, not least of which is the necessary simplification of a complex system in which the focus is on the results rather than the mechanisms of dissolution. Control of temperature and pH at values not unlike those in natural lake waters creates a dissolving medium in which the whole process of dissolution can be regularly monitored over a convenient period.

The results are intended to apply to problems of preservation as a whole, which is an interplay of the effects of dissolution and breakage. It is unrealistic and impossible to separate the two parallel processes as dissolving frustules break up more readily, and broken frustules dissolve more rapidly, but necessary to simplify tackling the much larger issue of preservation. The role of breakage will be minimised in these dissolution experiments, which can only provide the answers to preservation questions as first approximations.

4.8.2 Applicability

Apart from problems relating to design, the application of dissolution indices to reconstruct assemblages can obviously only be made for those taxa which are still identifiable in the sample after dissolution. Disappearance from an assemblage not only reflects complete dissolution of valves, but removal of characteristics allowing positive identification. Distinctive shapes (such as *Cymbella*, *Mastogloia* and some *Navicula* centres, and *Cyclotella* discs), which are otherwise featureless, can nonetheless be clearly read as taxonomic signatures, under conditions of degradation at which other taxa remain anonymous. Breakage of weakened valves, for species which depend on a central area for identification, likewise leads to loss of countable individuals in itself, apart from the further effect of promoting dissolution from newly exposed areas.

4.8.3 Methodological aspects

The relevance of an experimental approach to the whole preservation question rests on the argument that there are distinct, stable differences between species which are greater than those within them, at least in the same population. Although most work on diatom, radiolarian

and foraminiferal preservation agrees with this as a basic working principle, differences within species are to be expected, if the expression of the frustule is as highly variable in other respects as it is in terms of overall dimensions within a population. Factors that might affect resistance to dissolution and breakage might be equally variable, such as specific surface area and metal ion abundance within the ultrastructure of the silica lattice.

Further than this, Mikkelsen (1980) has suggested that the marine diatom *Coscinodiscus nodulifer* shows differences in resistance with latitude, high latitude populations dissolving in a morphologically and proportionately different way to low latitude samples, based on two replicate sample counts of 300 valves. This has cautionary implications for attempts to infer global rankings from regional data sets, especially if such significant variation exists at smaller scales, between lakes within a region or over time within a lake. Diatom robustness may reflect changes in water conditions in response to major and minor parameters (eg Paasche et al 1975) from dissolved silica levels to trace metal content.

Chapter 5
Diatom dissolution: experimental results

5.1 The controlled dissolution of NGP material

5.1.1 Introduction

Two experiments were carried out on a total of eleven synthetic assemblages of cleaned diatom valves, in November 1992 (6 assemblages, A-F) and February 1993 (5 assemblages, G-K), according to the method outlined in Chapter 4. An initial sample was taken for each mixture to act as a control (sample 1). Subsequent dissolution was monitored over the course of several weeks by estimating microsphere to diatom ratios counted using an inverted microscope, which in part determined the timing of successive samples. In the first experiment, 15 samples were taken from each assemblage, and in the second, thirteen. For each assemblage from each experiment, eight different samples (taken at the same time within each experiment) were chosen for detailed counts, and LM and SEM micrography.

The table below (5.1) gives the times at which each sample was taken. Those used for further analysis from each experiment are printed in bold.

Each experimental ("synthetic") assemblage was made up by mixing up to seven "natural" samples from living communities or surface sediments (cleaned, but without microspheres). These were mixed in proportions that had been calculated to allow the final mixtures to be dominated by only a few taxa, although the list of taxa that could be expected to be encountered was much longer. Before adding to dissolution flasks, checks were made on the assemblages for major diatom constituents and abundance (by counting a subsample with microspheres), to confirm that the proportions, and abundance were close to the ideal (based on original counts with microspheres on subsamples of the natural samples).

The quantity of diatoms that were included in each dissolution flask was chosen to be as large as possible below the ceiling set by the saturation concentration of the solution, and could only be reliably judged by completely dissolving subsamples of each assemblage of known diatom content (using microspheres) and measuring the silica content using spectrophotometry. Finally, microspheres were added to each assemblage and the mixture pitched into flasks, and immediately sampled to provide the control sample involving the same processing techniques used for subsequent subsamples.

Table 5.1

	Experiment 1		Experiment 2	
Sample	Days	Hours	Days	Hours
1	0.05	1.2	0.02	0.05
2	0.1	2.5	0.26	6.25
3	0.38	9	0.9	21.5
4	1.13	27	1.9	45.5
5	2.27	54.5	2.95	70.75
6	3.20	76.75	4.08	98
7	4.42	106	6.08	146
8	5.4	129.5	7.96	191
9	7.55	181.25	13.13	315
10	10.4	249.5	17.08	410
11	14.35	344.5	22.13	531
12	25.35	608.5	32.04	769
13	27.31	655.5	49.23	1181.5
14	28.31	679.5	---	---
15	31.15	747.5	---	---

Certain taxa were also selected to act as points of control and comparison between different assemblages. Several control taxa were included in most assemblages, chosen partly on account of their abundance and proportion in a natural sample, but more importantly on those initially thought to be relatively robust and easy to identify throughout the dissolution process, for example *Amphora libyca*, *Navicula oblonga*, and *Cyclotella meneghiniana*. Other taxa were also common to several assemblages above initial threshold levels, such as *Nitzschia palea* and *Nitzschia frustulum* in the first experiment, which, although relatively weakly silicified, could act as points of reference during the early phases of dissolution. The relationships between different assemblages, and experiments, is discussed in the section on ranking systems.

Some assemblages also included the same taxa, but from different original samples and lakes. In this way it was hoped to see if major differences in dissolution behaviour occurred within a taxon as well as between taxa.

5.1.2 Population decline

Figure 5.1-5.4 depict diatom abundance decline during the course of the first experiment (5.1 & 5.3) and second experiment (5.2 & 5.4), in terms of absolute numbers and percentage changes over time for ten of the eleven assemblages. In the second experiment, population changes could not be followed reliably using microspheres for assemblage H, on account of the dominance of very large taxa in the assemblage (particularly *Campylodiscus clypeus*) which effectively hid smaller valves and microspheres despite several attempts to resettle them. This also lead to problems during analysis under LM.

Initial numbers reflect the availability of material and the silica content of each assemblage. The exponential decline of the abundance of diatom valves agrees with the evidence of the preliminary experiment and the theoretical behaviour of solid silica dissolution, inversely proportional to the rise of dissolved silica in solution.

In the first experiment, for assemblages B and F in particular, diatom abundance decline was noticeably slower than the other populations in the same and subsequent experiment. Regression analysis of the diatom decline in the first six assemblages suggested that the time taken for the assemblages to reach 10% or 5% original numbers at the prevailing rates for these two assemblages would be from about 90-130 days (table 5.2), which was considered far beyond the original time period planned. Given that by this time only about 20-40% of the other populations were remaining, it was decided to increase the rate of dissolution for all samples to keep the experiment within a reasonable time period, by increasing the temperature in the water bath to 40°C.

Figure 5.1

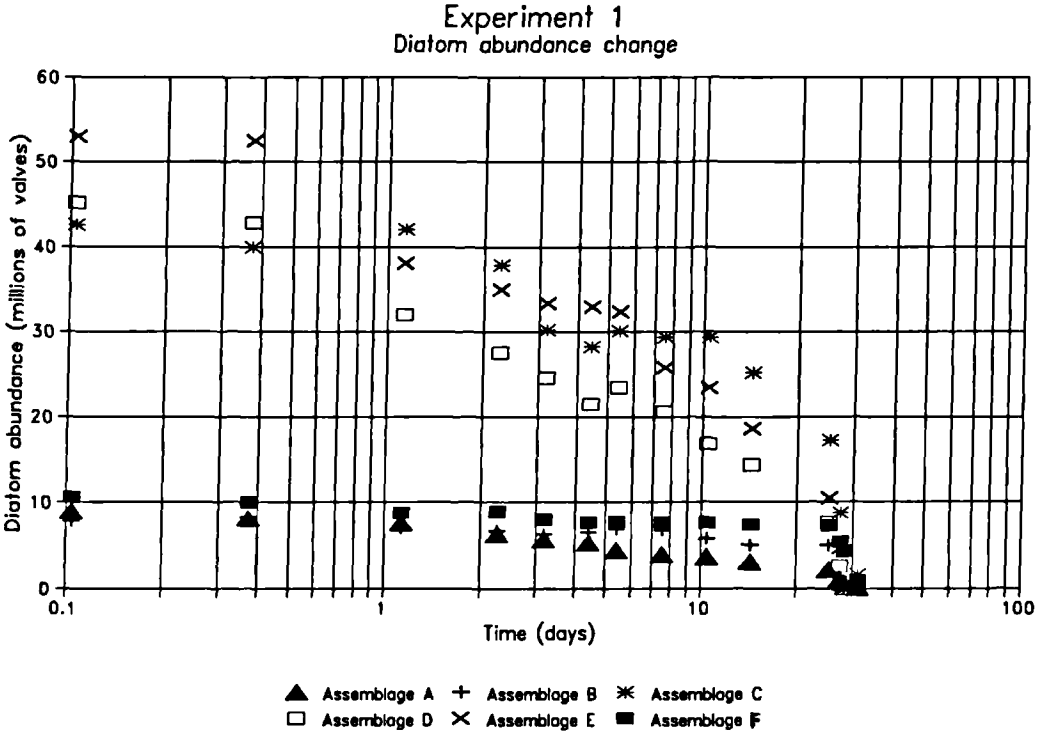


Figure 5.2

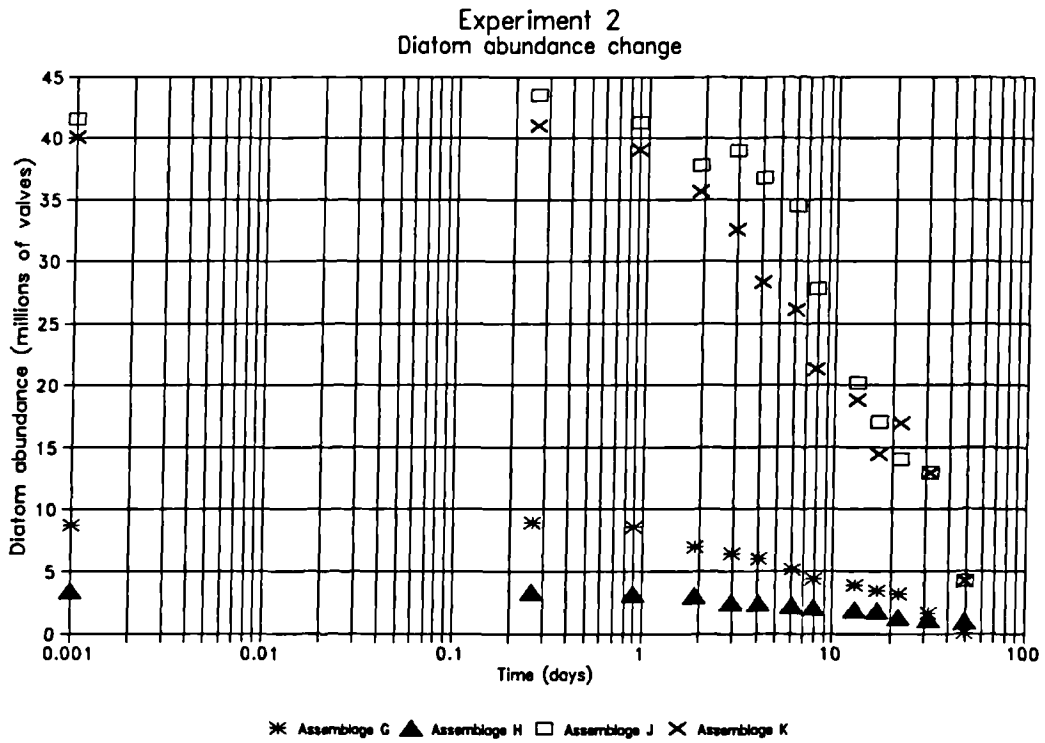


Figure 5.3

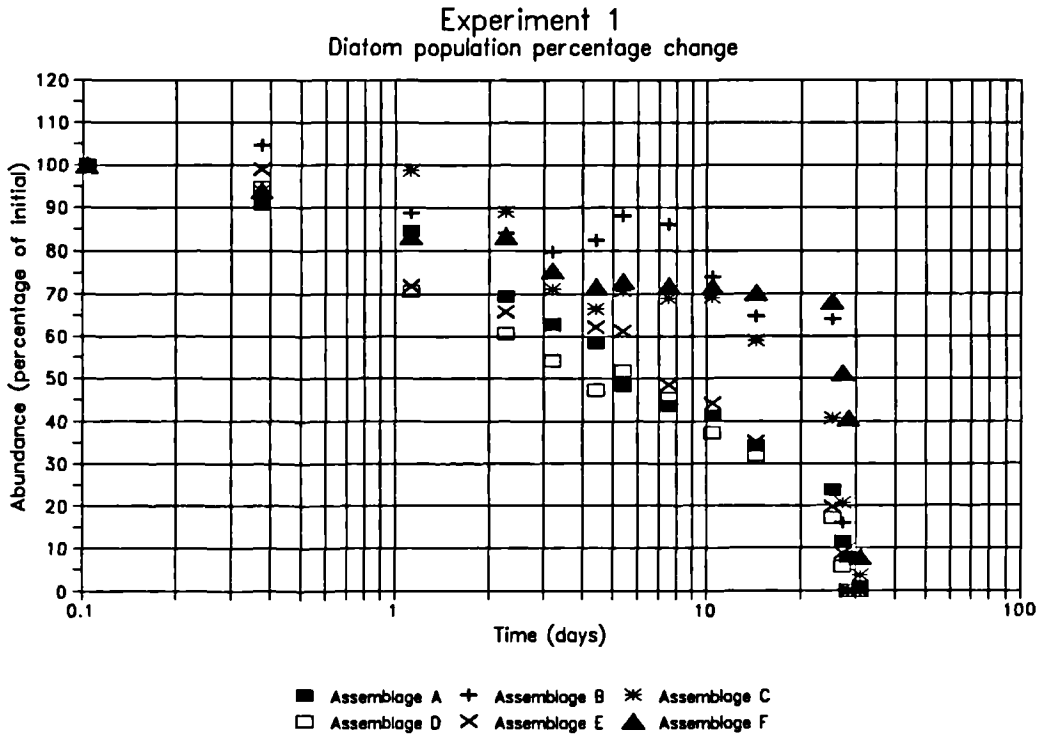


Figure 5.4

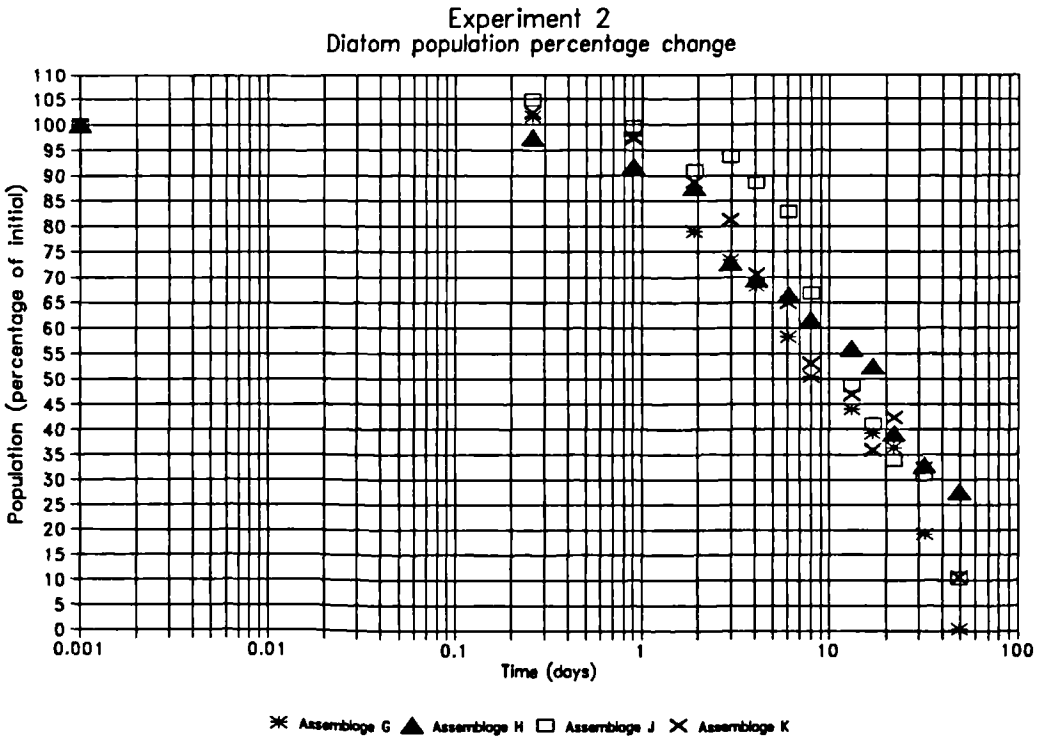


Table 5.2 Regressions of population against time (Experiment 1)

Regressions							Days to reach:	
y=ax+c	Dep y	Coeff a	Indep x	Constant c	R^2	Observations	Pop=10%	Pop=5 %
A1	ln(%pop)	-0.07	Time	4.46	0.90	10	29.00	38.34
A2	ln(%pop)	-0.03	Time	4.56	0.75	10	87.76	114.67
A3	ln(%pop)	-0.03	Time	4.52	0.72	10	64.34	84.46
A4	ln(%pop)	-0.07	Time	4.38	0.85	10	28.28	37.69
A5	ln(%pop)	-0.07	Time	4.46	0.90	10	32.15	42.49
A6	ln(%pop)	-0.02	Time	4.47	0.60	10	103.55	136.65

Altering the temperature is the best way of changing the rate in a controlled way. Dissolution at this increased rate will not affect the outcome or relative dissolution behaviour of taxa, and does not affect the purpose of the experiment, which was to dissolve diatoms sequentially; but it does affect the dissolution rate constant, k_2. All samples were treated the same way within the experiment to preserve comparability as far as possible. In the second experiment, experimental conditions were unchanged and dissolution continued for 7 weeks, by which time between 2% (assemblage G) and 25% (assemblage H) of original valve numbers remained.

5.1.3 Dissolved silica concentrations

Dissolved silica levels were measured in the supernatant solutions for each sample taken, from which the percentage of solid silica left in the sample was calculated from known total solid silica content of each assemblage (Chapter 4). Figures 5.5 and 5.6 show the relationship between estimated abundance decline and silica loss for experiment 1 (figure 5.5) and experiment 2 (figure 5.6).

Experimental dissolution behaviour can be considered in terms of the dissolution rate equation (equation **(1)** in Chapter 4):

$$\frac{dC_{sol}}{dt} = k_2 . (C_{sat} - C_{sol}) . S \qquad (1)$$

where:

dC_{sol}/dt is the rate of silica dissolution per unit time, in moles.cm^{-3}.sec^{-1};
k_2 is the rate constant in cm.sec^{-1};
C_{sat} and C_{sol} the value of the saturated and unsaturated solutions respectively, both in moles.cm^{-3};
S is the surface area of the available solid per unit volume of solution, in cm^2.cm^{-3}, or cm^{-1}.

Dissolution rates vary between assemblages even under the same experimental conditions and the increase in temperature in the first experiment increases dissolution by altering the rate constant (k_2). The individual rates of silica dissolution can be expected to vary between each assemblage as C_{sol} values will increase at different rates depending on the specific surface area of silica available. At the initial time, rates of silica dissolution are theoretically directly

Figure 5.5

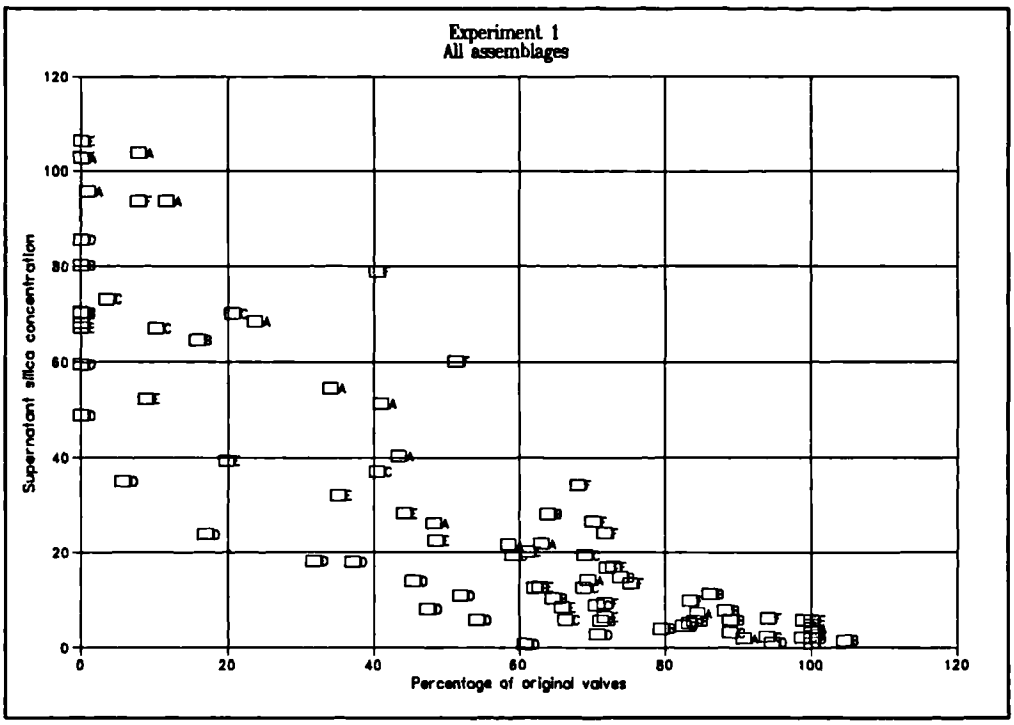
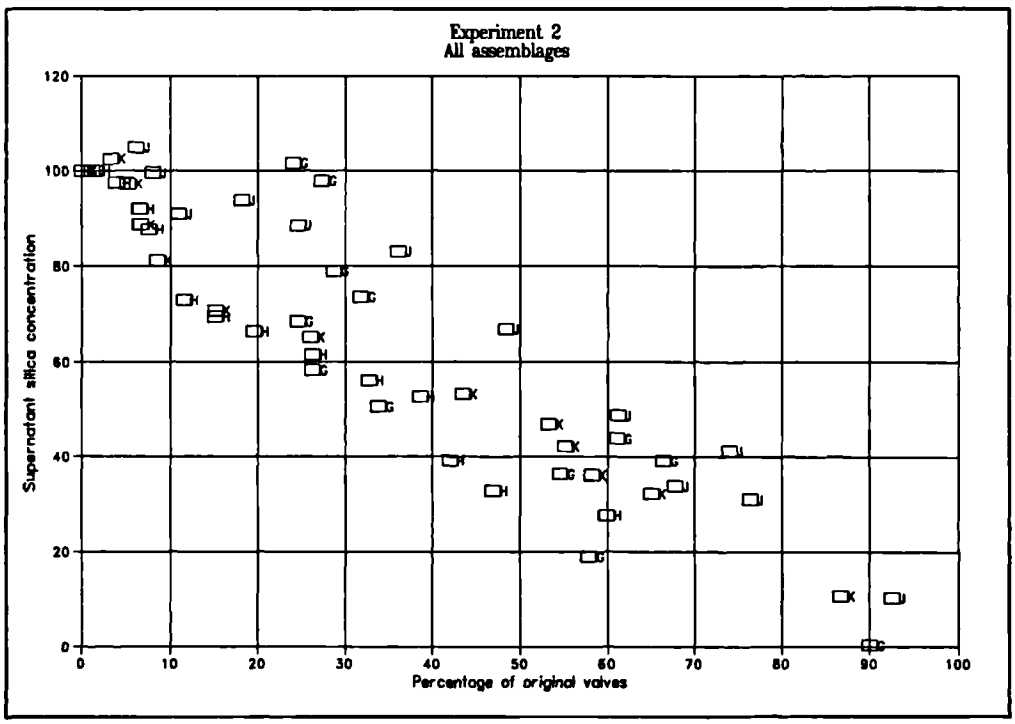


Figure 5.6



proportional to **S**, as the C_{sat} and k_2 terms in the equation are constant at given experimental conditions. Comparing initial silica dissolution rates can provide a means of estimating relative values of **S** for each fresh assemblage, and by implication changes in the ratios over time (given C_{sol} values). Unlike total silica content (*e.g.* Einsele & Grim 1938, Sicko-Goad *et al.* 1984), specific surface areas cannot be readily deduced from gross morphometric measurements. Dissolution rate tends to decrease over the course of the experiment as specific surface area of the assemblages and degree of undersaturation of the solution decrease (Kamatani *et al.* 1988, Lawson *et al.* 1978).

5.1.4 Assemblage composition changes (figures 5.7-5.25)

For each assemblage, eight samples were counted under LM at x1000 to at least 400 valves where possible, which became difficult for some later samples. In the case of assemblage H, counts were made at x600 due to field of view problems with very large *Campylodiscus* valves, which precluded accurate counts of smaller forms. Counts were made to 300-400 of the five taxa of importance in this mixture, namely two *Campylodiscus* taxa, *Anomoeonis costata*, *Surirella ovalis* and *Su. striatula*, and all analysis involving this assemblage relates to what are, in effect, counts outside the sum.

All counts were made recording "dissolution stages" (see Chapter 4) for each taxon, by which each valve encountered was classed according to its state of dissolution into one of up to four categories ("stages"), depending on the number of distinct stages valve morphology and appearance underwent during dissolution from a pristine state (stage 1) to complete disappearance (or rather unidentifiability). Photomicrographs of these stages are reproduced in Appendix 1 for the main taxa, under both SEM and LM, based on examination of material from the same samples used for LM counts. Dissolution stages were identified for taxa prior to detailed LM analysis by looking at the dissolution spectrum represented by the time series of samples for each taxon individually.

The following graphs depict the changes in the major components of each assemblage over time, represented by sample number increasing from left to right (figure 5.7-5.25). Although such data are closed, as valve numbers of any taxon cannot increase, they represent the relative rates of population decline of each individual form, which can be equated with resistance to dissolution. Fragile species, such as *Nitzschia palea*, *Ni.* aff. *fonticola*, *Ni. frustulum* (assemblages A-F), and small centric species (*Cyclostephanos tholioformis* and *Stephanodiscus minutulus* in assemblage G) tend to disappear rapidly in all situations, while relative frequencies of more robust taxa (such as *Amphora libyca*, *Navicula oblonga*, the cysts of *Chaetoceros* sp. and large centrics *Cyclotella quillensis* and *Stephanodiscus niagarae*)

Figure 5.7

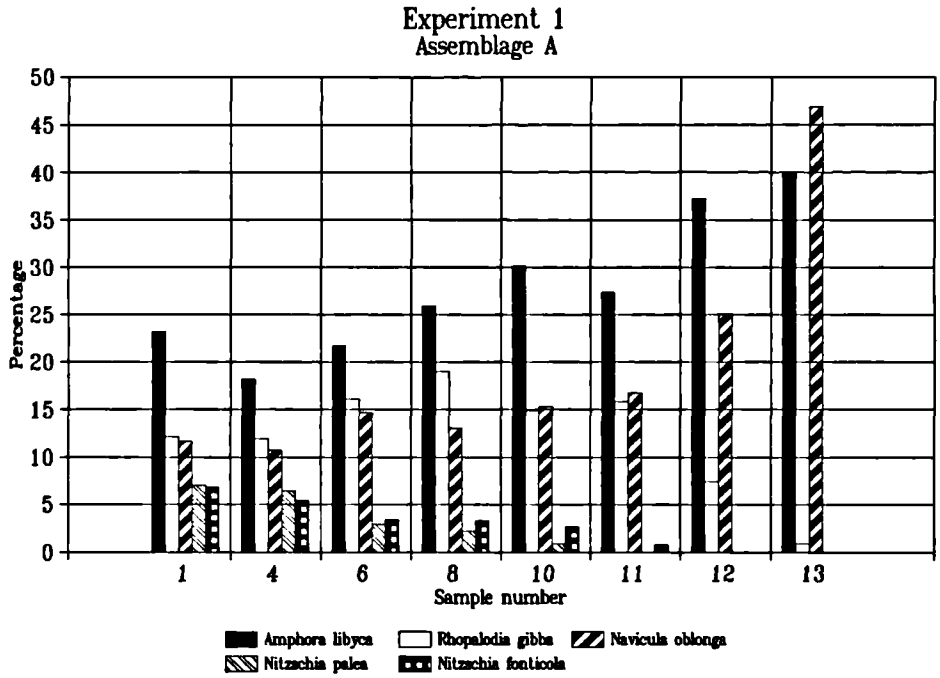


Figure 5.8

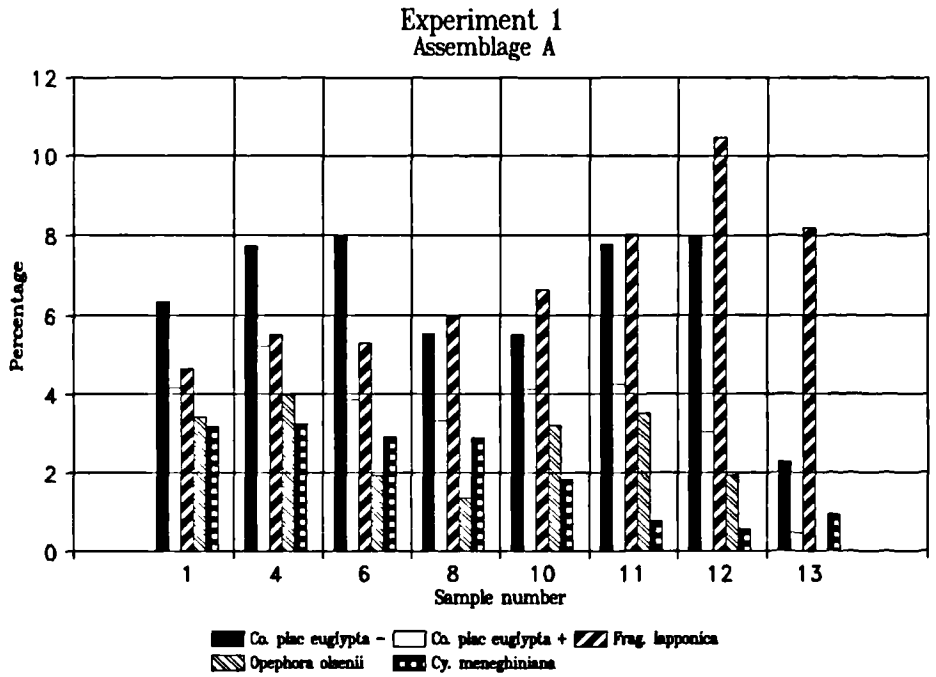


Figure 5.9

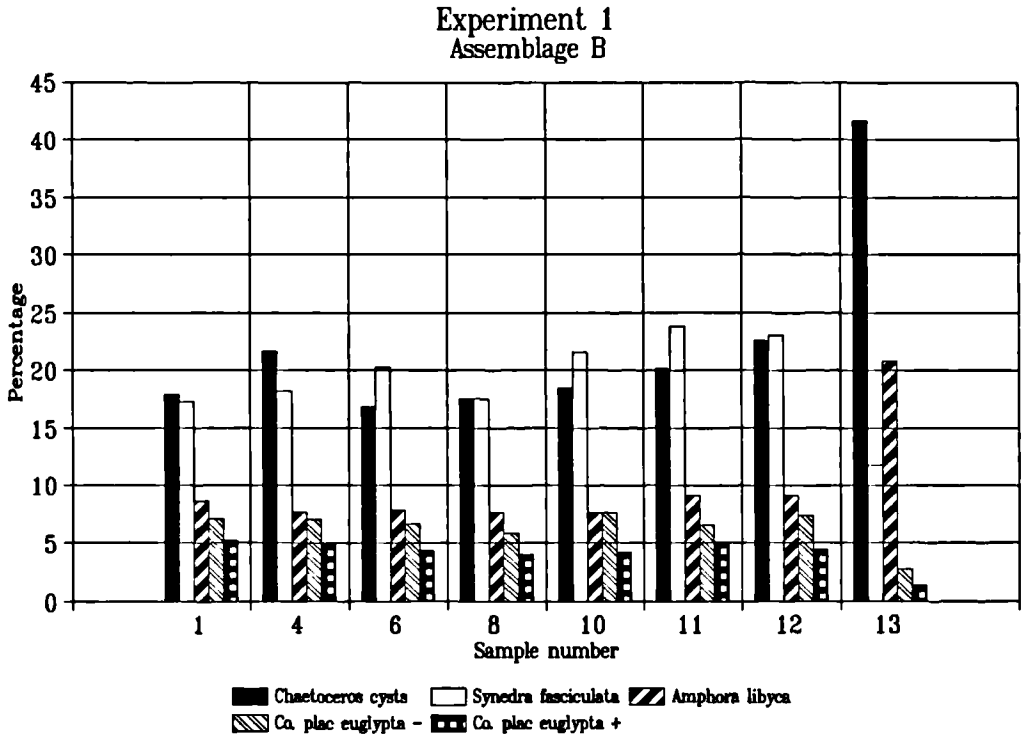


Figure 5.10

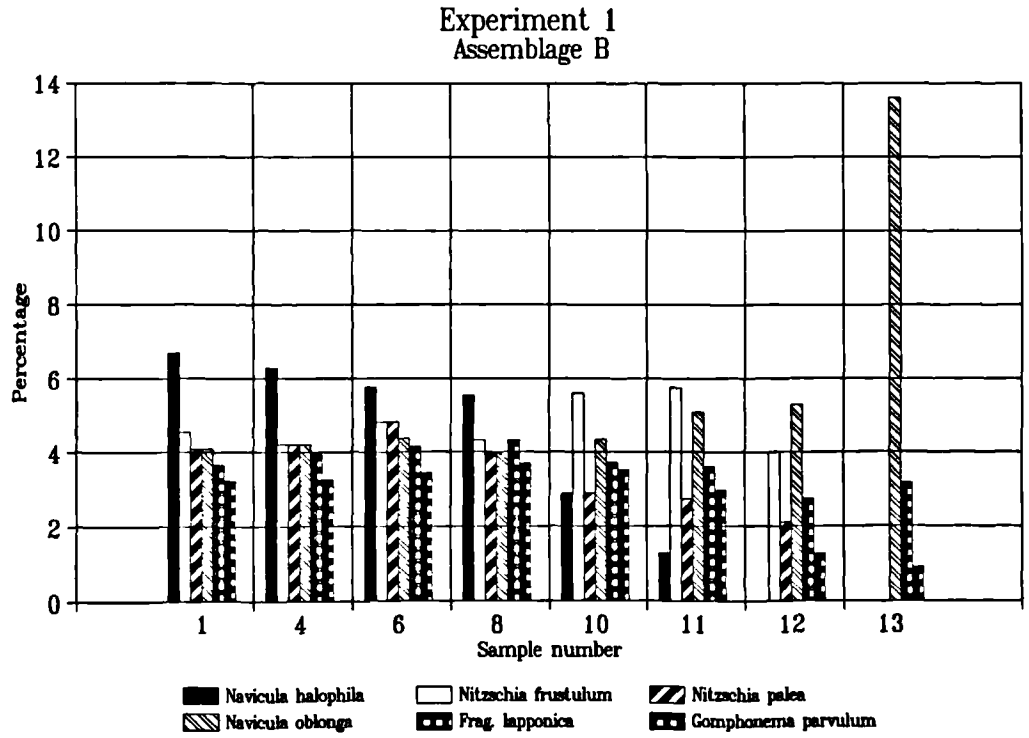


Figure 5.11

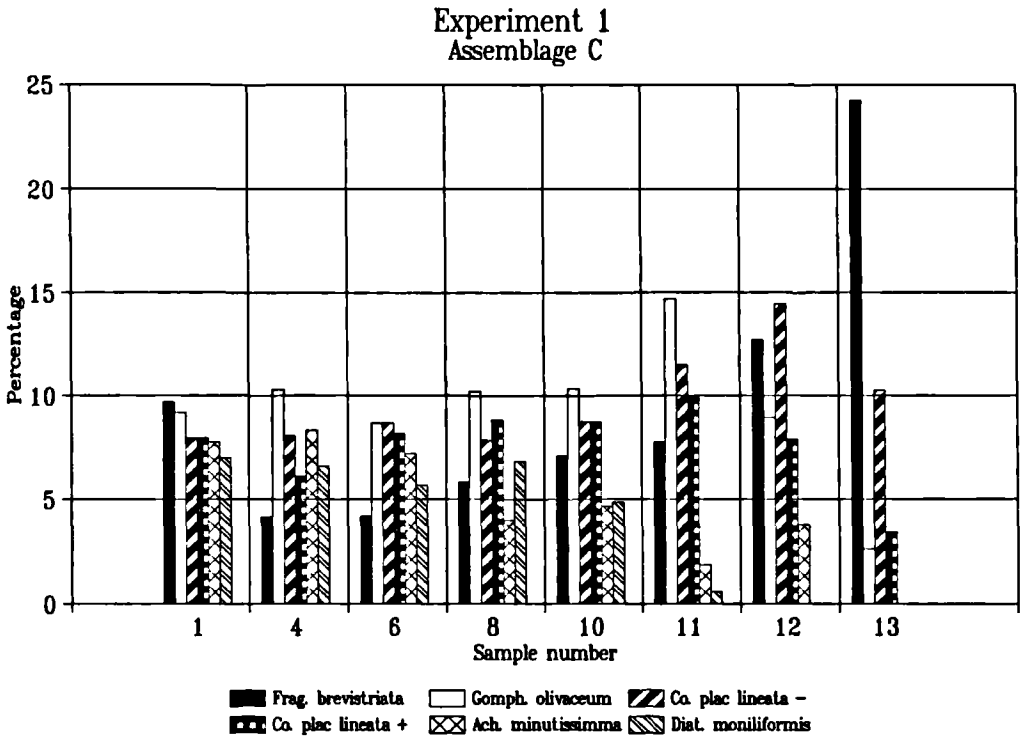


Figure 5.12

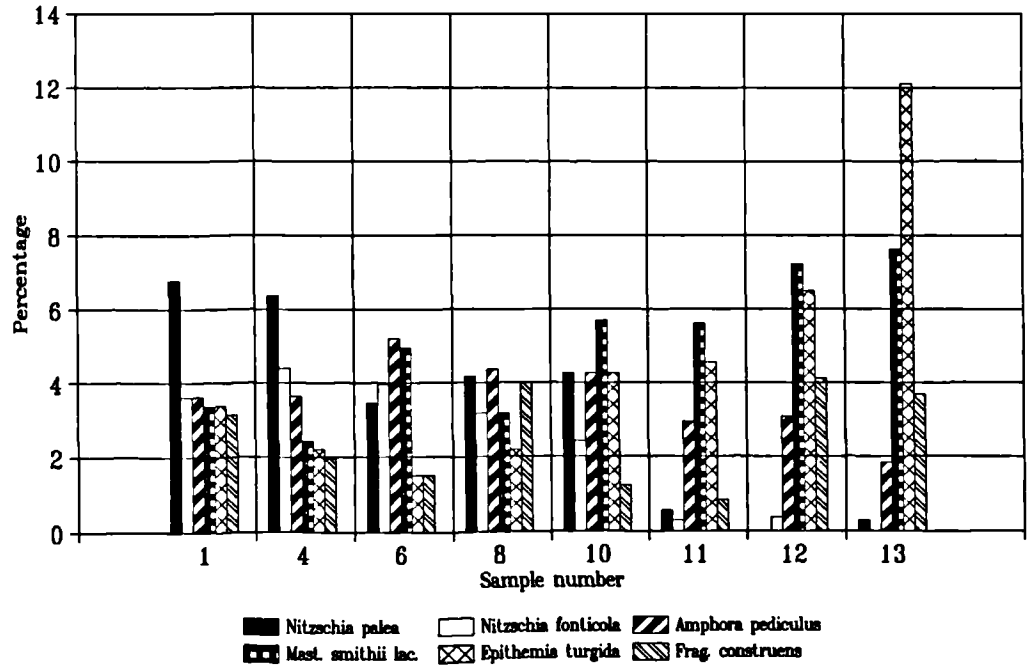


Figure 5.13

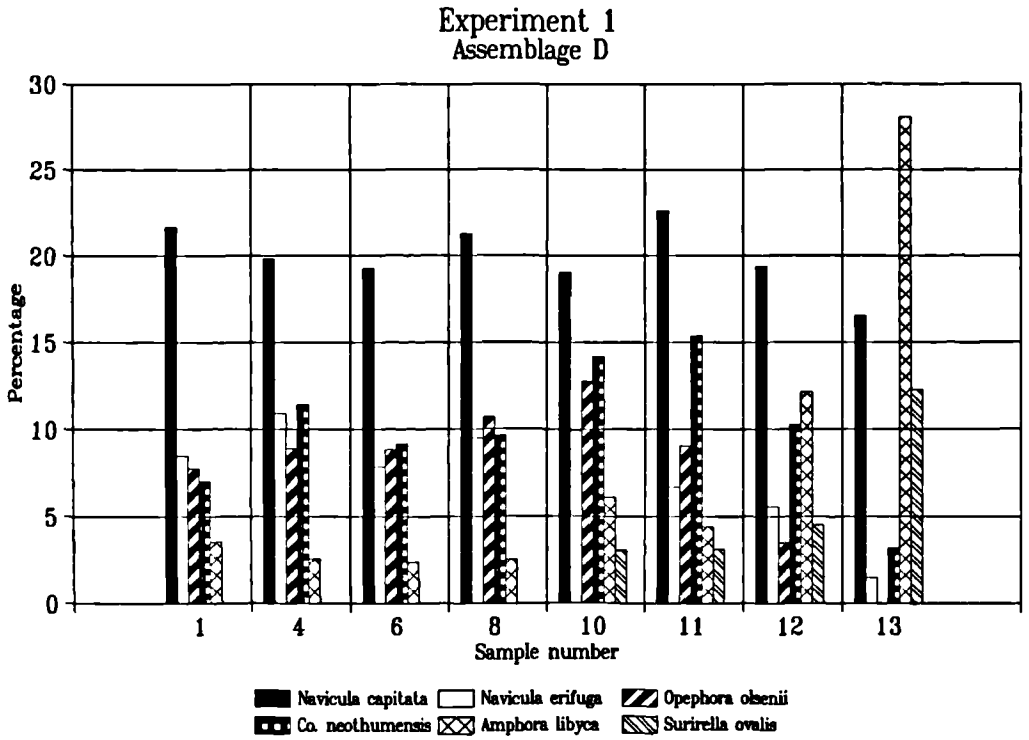
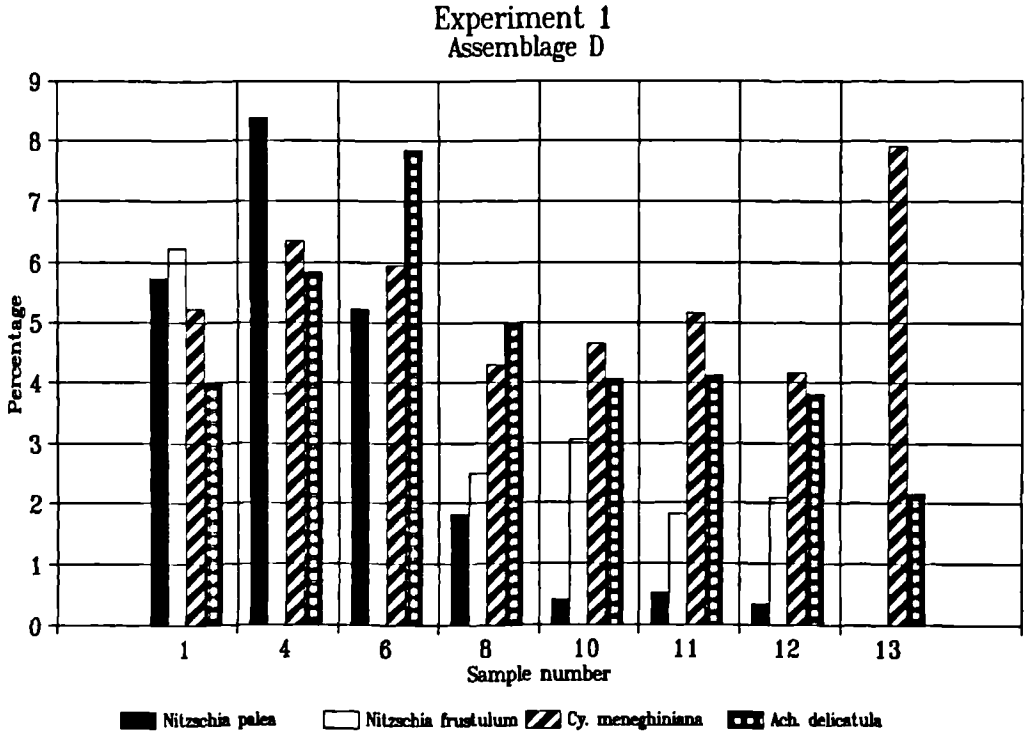


Figure 5.14



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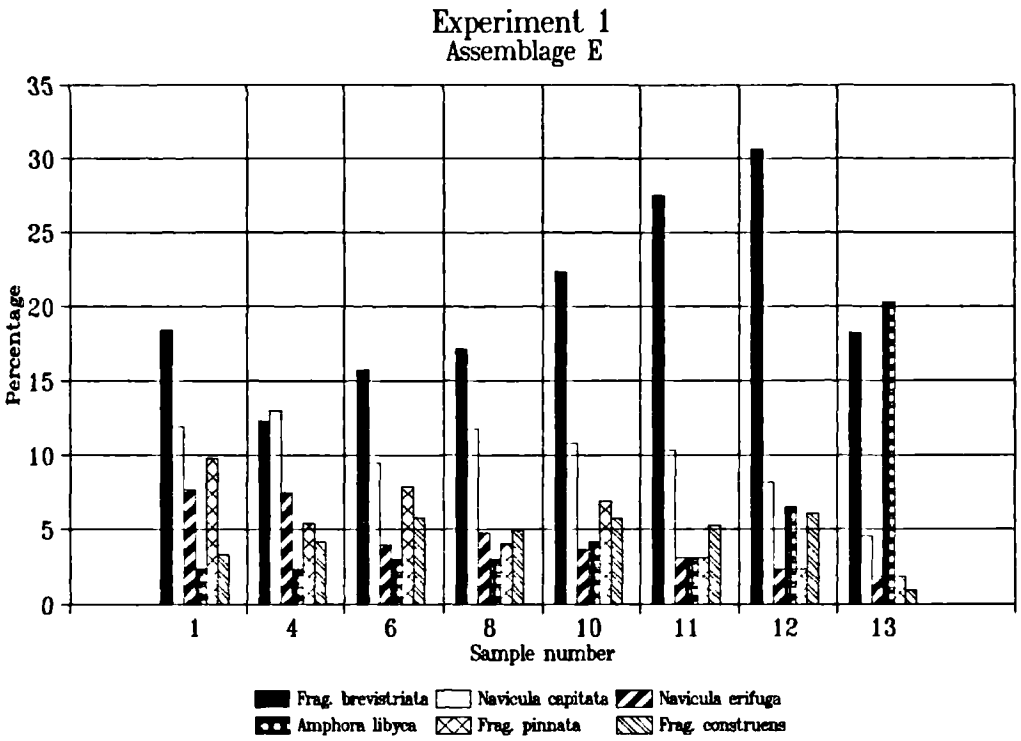

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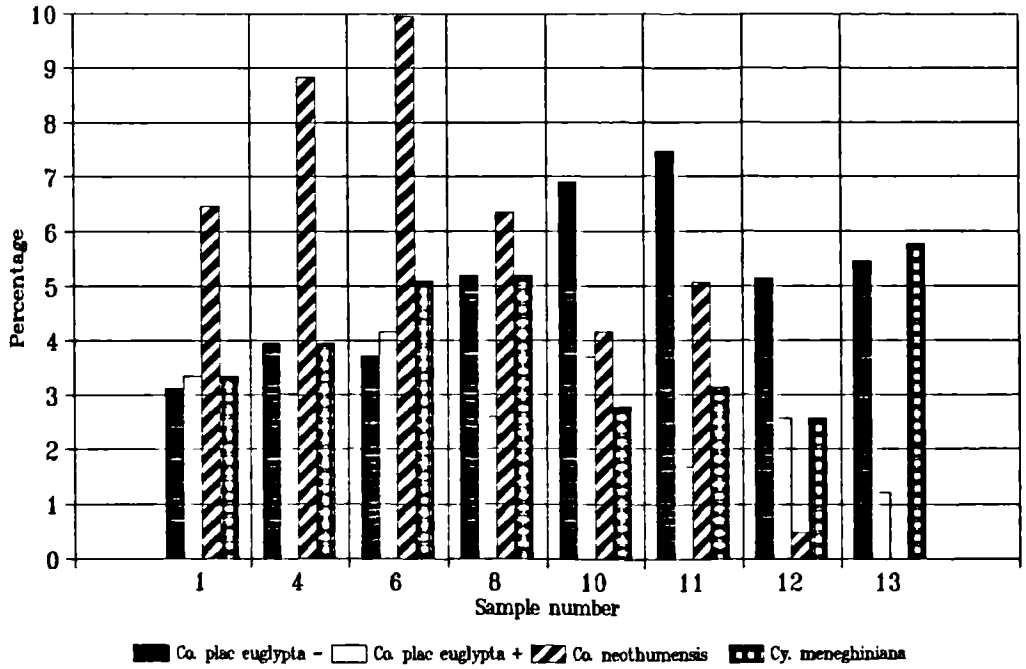


Figure 5.17

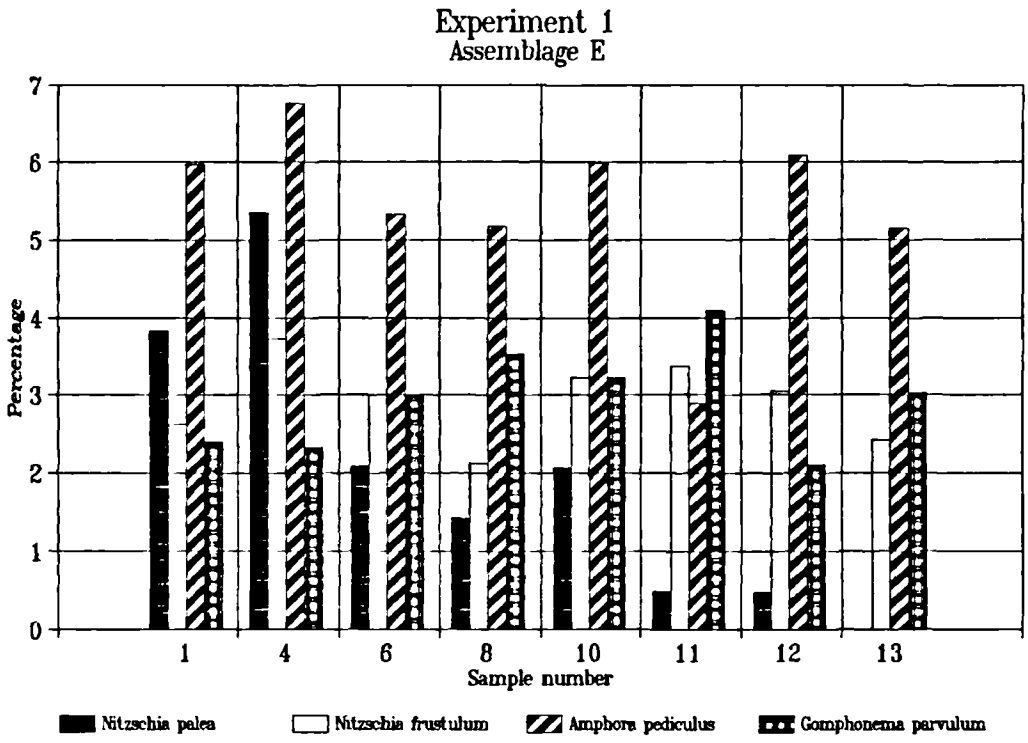


Figure 5.18

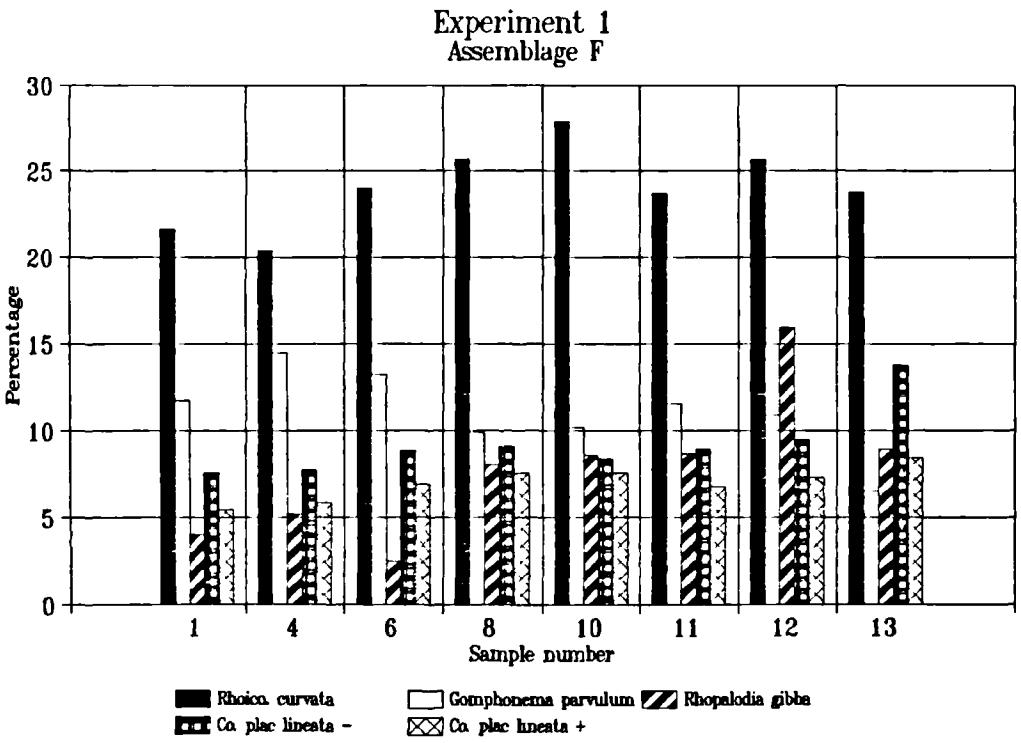
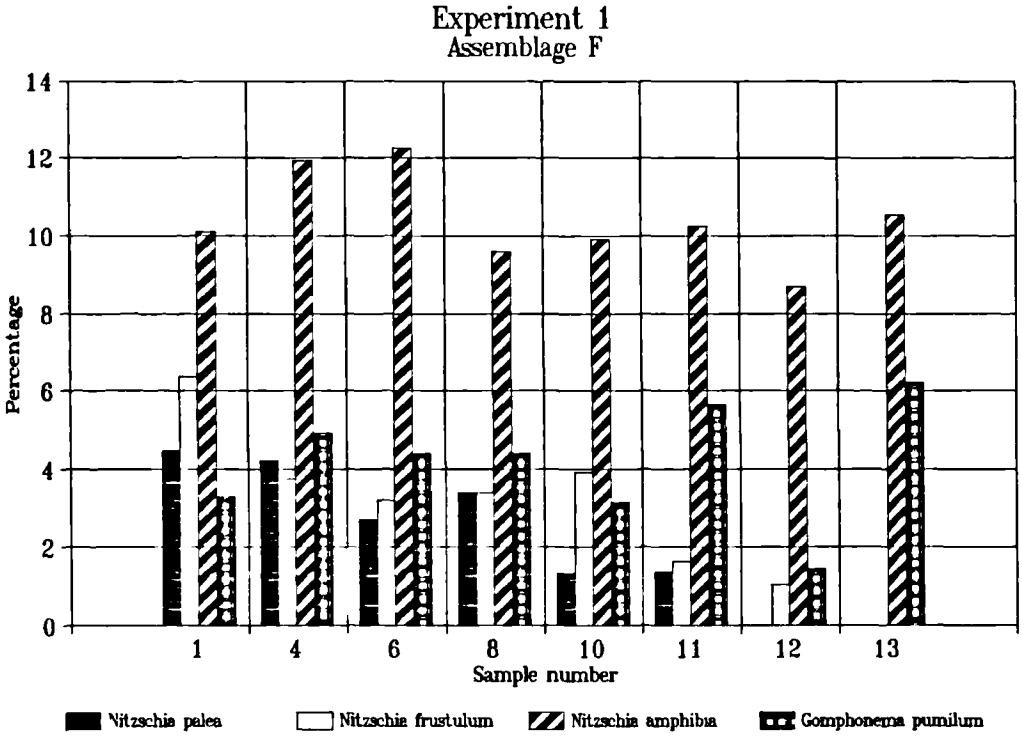


Figure 5.19



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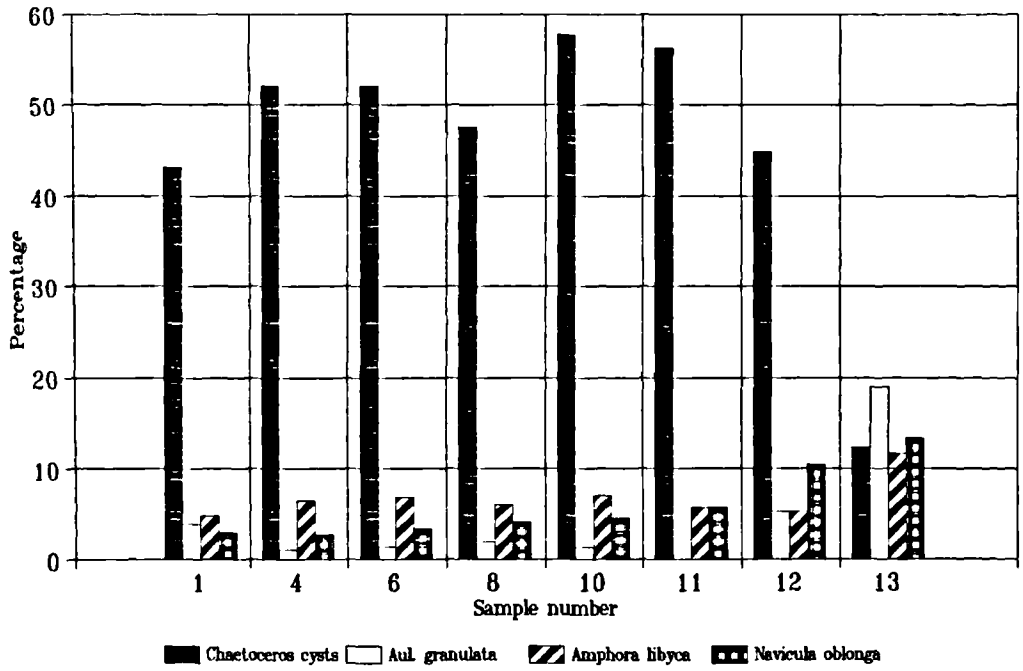

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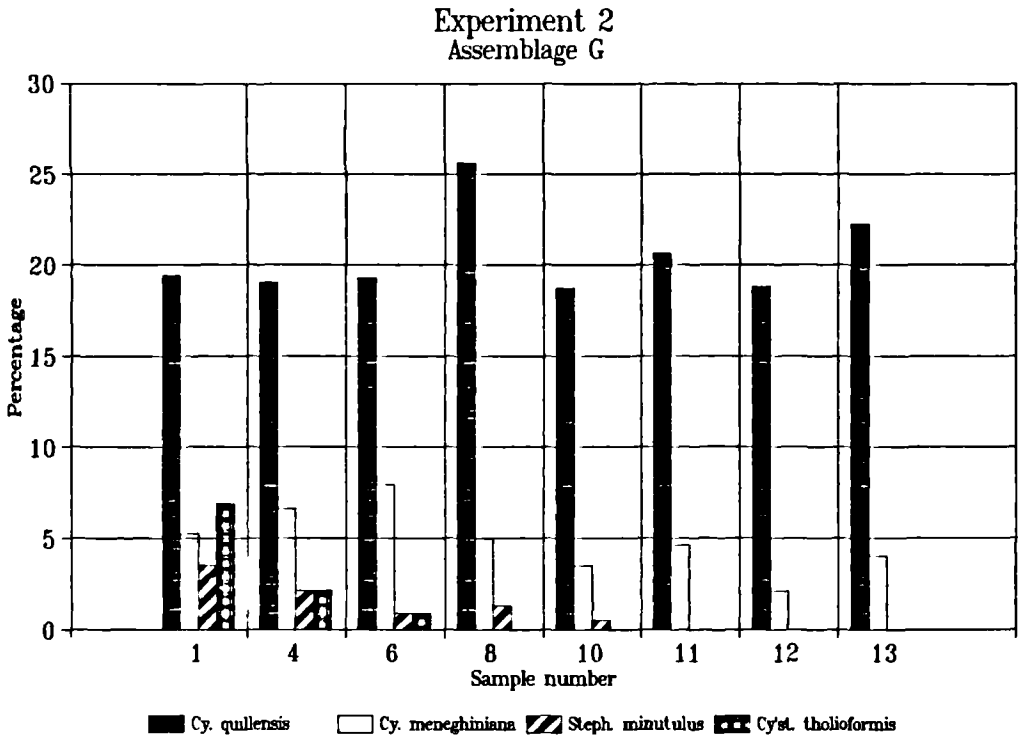


Figure 5.22

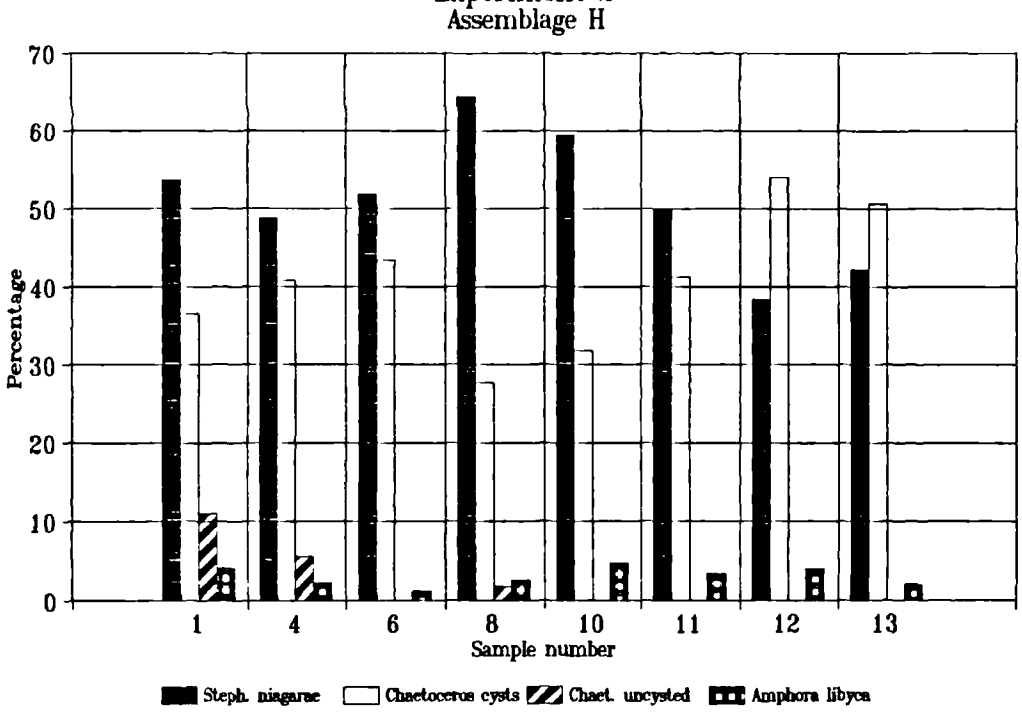


Figure 5.23

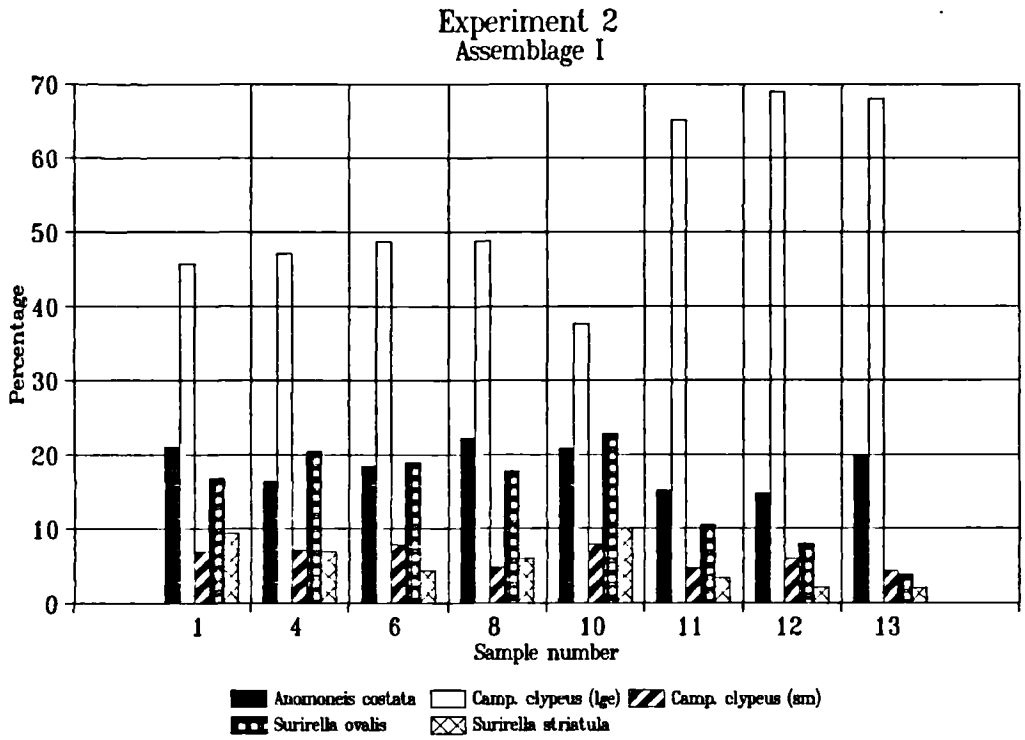


Figure 5.24

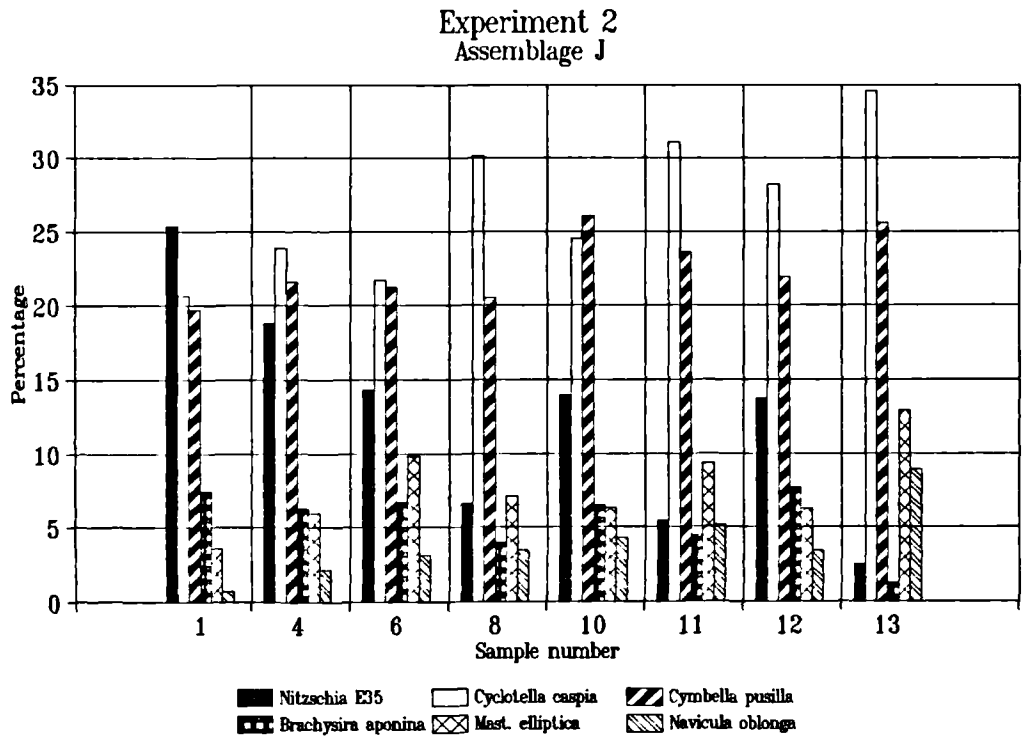
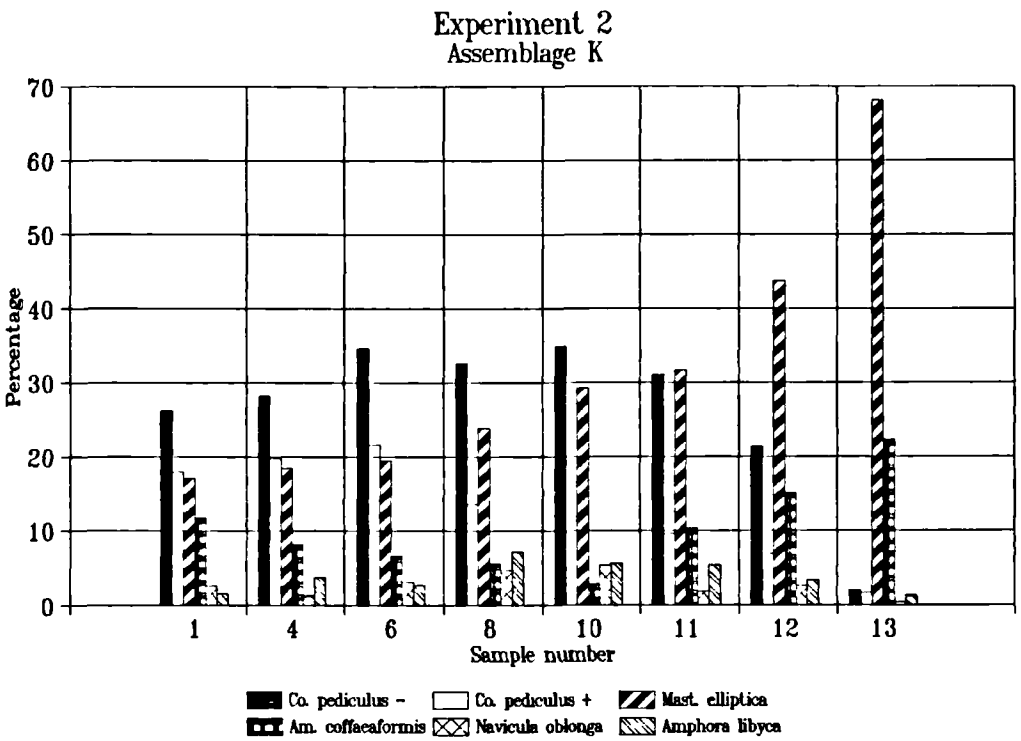


Figure 5.25


Experiment 2
Assemblage K
Percentage
70
60
50
40
30
20
10
0
1
4
6
8
10
11
12
13
Sample number
Co. pediculus -
Co. pediculus +
Mast. elliptica
Am. coffaeaformis
Navicula oblonga
Amphora libyca

correspondingly increase.

The only form of *Chaetoceros* cells found in surface sediments was as cysts (assemblages B and G). Uncysted *Chaetoceros* cells were found in samples collected from a bloom in Coldwater Lake in the 1992 field season, as a minor component of a dominantly encysted population. Material from this sample was included in assemblage H. Results from assemblages B, G and H suggest that one reason for the absence of uncysted cells in surface sediments is the extreme susceptibility of this form relative to the obviously robust cyst usually encountered in sediments.

Results presented in this way are difficult to compare directly from one assemblage to the next, as the behaviour of each taxon as a percentage of the whole depends on the susceptibility of the rest of the assemblage as well as its intrinsic robustness. This "solubility competition" can be demonstrated by *Amphora libyca*. In assemblages A, B & G for example, this species tends to increase in proportion over time, while in assemblages H & K the trend is far less certain, although there are undoubtedly errors associated with counting at lower percentages. Such variation cannot be explained by differences in the growing conditions of this species as the source of the great proportion of this taxon in these assemblages is from one live sample.

5.2 Ranking taxa

5.2.1 Using percentage data (figures 5.7-5.25)

5.2.1.1 Mikkelsen's ranking system

Mikkelsen's ranking method (Mikkelsen 1980) uses ratios of percentage occurrence of sequential samples to initial values to establish a ranking for each sample, in descending order from largest to smallest ratio implying most to least resistant species. This method was applied to results from these dissolution experiments according to equation **(3)** from Chapter 4:

$$r_i = \frac{n_{i(t)}}{n_{i(0)}} \qquad (2)$$

Ratios were calculated for all taxa in all samples with an initial value of occurrence of 3% or over, with sample 1 as the initial, except in a few cases where robust taxa only crossed the 3% threshold level in later samples, for which the initial sample was the first occurrence over 3%.

This threshold allowed for at least 70%, and often a much greater proportion, of the total diatoms counted to be included in the ranking procedure. Species were ranked from 1 upwards as susceptibility to dissolution increased. Taxa with tied ranks were given the same ranking, which was taken as the highest rank covered by the tie (for example, three species equally ranked as least resistant in an assemblage of 10 species would be given the tied value of 10th, rather than 8th).

Rank ordering was thought to have been approximately established in most cases by sample 4, as between 10-40% (experiment 1) and 10-20% (experiment 2) of total diatom populations had been lost from assemblages, after about 2 days of dissolution. This sample was used as the first point of comparison in the ratio calculations, and so the rankings for all taxa that were over 3% in sample 1 are derived from a series of seven observations for each assemblage.

Some taxa had to be pooled for this analysis as it was difficult to identify raphid and rapheless valves as dissolution proceeded (*e.g. Ach. minutissima*), and in some cases the differences between varieties became blurred (such as *Achnanthes delicatula* & var. *hauckiana* and *Fragilaria brevistriata* & var. *inflata*). Some identifiable taxa (such as *Aulacoseira granulata* & *Au. granulata* var. *angustissimma*) were not abundant enough to be included separately and the decision to include them in a ranking overrode the desire to keep all distinct taxa separate. The results for this taxon may not represent either accurately but does at least give an impression of the average behaviour of the two forms. *Rhoicosphenia curvata* was pooled as in many early samples the girdle view of valves accounted for the vast majority of valves seen, to the extent that using the proportions of raphe and rapheless valves counted to divide the girdle count could not be used as a reliable guide.

Using the ranks directly provides two systems of ordering taxa, either as average rank in each assemblage ($\mathbf{a_1}$, the sum of individual rank positions, divided by the number of observations) or as final rank ($\mathbf{a_2}$), whereby these average ranks are themselves ordered to give a whole number rank for each taxon in each assemblage. These raw data can then be used directly to produce a ranking of all taxa, in order of increasing rank (decreasing resistance), again with tied ranks being given the same high value. Species can be ordered by comparing the average of $\mathbf{a_1}$ and $\mathbf{a_2}$ values for all occurrences across all assemblages. The two ranking systems produced from the raw rank data are shown in table 5.3, susceptibility to dissolution increasing with rank number.

5.2.1.2 Discussion

Although there is much similarity between the order, as would be expected, there are important

Table 5.3 - Experimental ranking (a_1 & a_2)

a_1		a_2	
Rank	**Taxon**	**Rank**	**Taxon**
1	Mastogloia elliptica	4	Anomoeoneis costata
2	Stephanodiscus niagarae	4	Mastogloia elliptica
3	Synedra fasciculata	4	Mastogloia smithii var lacustris
4	Anomoeoneis costata	4	Synedra fasciculata
6	Campylodiscus clypeus - large	6	Rhopalodia gibba
6	Campylodiscus clypeus - small	6	Stephanodiscus niagarae
8	Chaetoceros cysts	7	Chaetoceros cysts
8	Rhopalodia gibba	8	Fragilaria lapponica
9	Gomphonema pumilum group	9	Navicula oblonga
11	Fragilaria lapponica	14	Achnanthes delicatula (all forms)
11	Mastogloia smithii var lacustris	14	Campylodiscus clypeus - large
12	Navicula oblonga	14	Campylodiscus clypeus - small
13	Surirella ovalis	14	Cocconeis placentula var lineata -
14	Achnanthes delicatula (all forms)	14	Gomphonema pumilum group
15	Surirella striatula	15	Surirella ovalis
16	Cyclotella quillensis	16	Amphora libyca
17	Amphora libyca	21	Chaetoceros - no cysts
18	Chaetoceros - no cysts	21	Cocconeis pediculus -
20	Cocconeis pediculus -	21	Cocconeis placentula var lineata +
20	Cocconeis placentula var lineata -	21	Cyclotella quillensis
21	Cocconeis placentula var lineata +	21	Gomphonema olivaceum
22	Cocconeis placentula var euglypta -	22	Cocconeis placentula var euglypta -
24	Aulacoseira granulata (all forms)	27	Amphora coffeaeformis
24	Gomphonema olivaceum	27	Amphora pediculus
27	Amphora coffeaeformis	27	Epithemia turgida
27	Ntzschia amphibia	27	Fragilaria construens
28	Rhoicosphenia curvata (all forms)	27	Surirella striatula
28	Cyclotella meneghiniana	28	Cyclotella meneghiniana
29	Cymbella pusilla	29	Gomphonema parvulum
30	Cocconeis pediculus +	33	Aulacoseira granulata (all forms)
31	Fragilaria construens	33	Cyclotella caspia
32	Epithemia turgida	33	Nitzschia amphibia
33	Gomphonema parvulum	33	Rhoicosphenia curvata (all forms)
34	Cyclotella caspia	36	Cocconeis pediculus +
35	Amphora pediculus	36	Cymbella pusilla
36	Opephora cf olsenii	36	Opephora cf olsenii
37	Brachysira aponina	37	Stephanodiscus minutulus

38	Fragilaria brevistriata (all forms)	38	Fragilaria brevistriata (all forms)
39	Stephanodiscus minutulus	41	Brachysira aponina
40	Navicula capitata var capitata	41	Cocconeis placentula var euglypta +
41	Cocconeis placentula var euglypta +	41	Cyclostephanos tholioformis
42	Cyclostephanos tholioformis	42	Nitzschia frustulum
43	Nitzschia frustulum	44	Navicula capitata var capitata
44	Nitzschia E35	44	Nitzschia aff fonticola var 1
45	*Nitzschia aff fonticola var 1*	45	Nitzschia E35
46	Navicula erifuga	46	Navicula erifuga
47	Cocconeis neothumensis -	47	Nitzschia palea
49	Achnanthes minutissima (all forms)	51	Achnanthes minutissima (all forms)
49	Diatoma moniliformis	51	Cocconeis neothumensis -
50	Nitzschia palea	51	Diatoma moniliformis
51	Navicula halophila	51	Navicula halophila
53	Cocconeis neothumensis +	53	Cocconeis neothumensis +
53	Fragilaria pinnata	53	Fragilaria pinnata

differences, and the position of some taxa are contrary to what observation and experience would suggest, for example the high position of *Achnanthes delicatula* (all forms) and uncysted *Chaetoceros* cells. The problem with using ranked data especially in its raw form is that the ordinal nature is inherently unsuited to comparing assemblages of different composition, where there are different numbers of taxa that are being ranked. For example, assemblage E has 15 taxa being ranked, while assemblages 8 and 9 have 4 and 5 taxa respectively. *Surirella ovalis* and *Su. striatula* in assemblage I, and uncysted *Chaetoceros* cells in assemblage H are ranked equal 5th and 4th ($\mathbf{a_2}$) as the least resistant to dissolution in their respective assemblages, but cannot be arbitrarily compared with taxa ranked similarly in other assemblages. Even the same taxa in different assemblages cannot be adequately used to correlate assemblages using these raw data without ambiguity and assumptions.

There are several ways of adjusting the raw data to reflect these assemblage differences which can improve the ranking, using inherently more reasonable and logical rules for comparing assemblages. The most useful examined here weighted the raw $\mathbf{a_1}$ and $\mathbf{a_2}$ ranks by dividing values by the sum of all ranks in each assemblage ($\Sigma \mathbf{r}$, where r is the rank), so that a rank of 4th in assemblage H was divided by 10 (0.4) and rank 4th in assemblage E was divided by 120 (0.033). In this way, taxa in larger assemblages were favoured over those from smaller. The results of this procedure are shown in table 5.4, increasing rank denoting decreasing robustness.

The ranking by this method is undoubtedly better than the raw values, although with no independent means of knowing what the ranking should be it is impossible to predict how close it is to reality, or how much better than raw ranking. Using ordinal ranked data does still create problems of correlation between assemblages, and there is still a significant arbitrary element in the weighting procedure. *Chaetoceros* cysts for example, are relatively susceptible to dissolution according to the weighted ranking, below *Achnanthes delicatula* in both cases, and below *Amphora coffeaeformis* with $\mathbf{a_1}$ weighted values. Anomalies like this suggest that ranked, ordinal values are not the optimum means of ranking species in different dissolving assemblages.

In a sense, $\mathbf{a_1}$ data are better for this ranking exercise, as these data are semi-ordinal, being the average of several samples' ranking observations, even though these individual within-assemblage sample rankings are strictly ordinal. The best type of approach is one based on interval data, and this can be applied to dissolution experiments by considering the actual ratios involved in Mikkelsen's ranking system.

The original percentage ratio for a taxon in any individual sample from an assemblage

Table 5.4 - Experimental ranking (a_1 & a_2, weighted)

$a_{1:\ weighted}$		$a_{2:\ weighted}$	
Rank	Taxon	Rank	Taxon
1	Mastogloia elliptica	1	Mastogloia smithii var lacustris
2	Synedra fasciculata	2	Synedra fasciculata
3	Mastogloia smithii var lacustris	3	Mastogloia elliptica
4	Fragilaria lapponica	4	Rhopalodia gibba
5	Rhopalodia gibba	5	Fragilaria lapponica
6	Amphora pediculus	6	Amphora pediculus
7	Gomphonema olivaceum	7	Navicula oblonga
8	Fragilaria construens	8	Gomphonema olivaceum
9	Navicula oblonga	9	Achnanthes delicatula (all forms)
10	Achnanthes delicatula (all forms)	10	Cocconeis placentula var lineata -
11	Cocconeis placentula var euglypta -	11	Fragilaria construens
12	Cocconeis placentula var lineata +	12	Cocconeis placentula var lineata +
13	Gomphonema pumilum group	13	Epithemia turgida
14	Epithemia turgida	15	Anomoeoneis costata
15	Cocconeis placentula var lineata -	15	Gomphonema pumilum group
16	Cocconeis neothumensis -	16	Cocconeis placentula var euglypta -
17	Fragilaria brevistriata (all forms)	17	Chaetoceros cysts
18	Cocconeis pediculus -	18	Cocconeis pediculus -
19	Navicula capitata var capitata	19	Fragilaria brevistriata (all forms)
20	Gomphonema parvulum	20	Amphora coffeaeformis
21	Amphora coffeaeformis	21	Gomphonema parvulum
22	Cyclotella meneghiniana	22	Cocconeis neothumensis -
23	Amphora libyca	23	Amphora libyca
24	Cocconeis placentula var euglypta +	24	Cyclotella meneghiniana
25	Navicula erifuga	25	Cocconeis placentula var euglypta +
27	Cocconeis neothumensis +	26	Cyclotella quillensis
27	Fragilaria pinnata	27	Cyclotella caspia
28	Chaetoceros cysts	28	Navicula capitata var capitata
29	Cyclotella quillensis	29	Opephora cf olsenii
30	Cymbella pusilla	30	Navicula erifuga
31	Cocconeis pediculus +	32	Cocconeis neothumensis +
32	Opephora cf olsenii	32	Fragilaria pinnata
34	Nitzschia amphibia	33	Cymbella pusilla
34	*Rhoicosphenia curvata (all forms)*	34	Cocconeis pediculus +
35	Cyclotella caspia	36	Nitzschia amphibia
37	Achnanthes minutissima (all forms)	36	Rhoicosphenia curvata (all forms)
37	Diatoma moniliformis	37	Nitzschia frustulum

38	Nitzschia frustulum	38	Nitzschia aff fonticola var 1
39	Aulacosiera granulata (all forms)	40	Achnanthes minutissima (all forms)
40	Nitzschia aff fonticola var 1	40	Diatoma moniliformis
41	Brachysira aponina	41	Nitzschia palea
42	Nitzschia palea	42	Brachysira aponina
43	Surirella ovalis	44	Aulacoseira granulata (all forms)
44	Navicula halophila	44	Navicula halophila
45	Anomoeoneis costata	45	Surirella ovalis
46	Nitzschia E35	46	Nitzschia E35
48	Campylodiscus clypeus - large	47	Stephanodiscus minutulus
48	Campylodiscus clypeus - small	50	Campylodiscus clypeus - large
49	Stephanodiscus minutulus	50	Campylodiscus clypeus - small
50	Stephanodiscus niagarae	50	Stephanodiscus niagarae
51	Cyclostephanos tholiformis	51	Cyclostephanos tholiformis
52	Surirella striatula	52	Surirella striatula
53	Chaetoceros - no cysts	53	Chaetoceros - no cysts

represents the competitive performance of that taxon in maintaining its initial share of the assemblage. These ratios (Mikkelsen's **r** values) can themselves be averaged over all occurrences for each assemblage for all taxa (called here ß values), which can then be compared directly to produce a ranking. Where taxa appear in more than one assemblage, the ß value is the average value for this ratio in all assemblages, as before.

The ß value ordering of taxa is given in table 5.5, and the individual taxon ß values from which the table is derived in figure 5.26. ß values above 1 represent species which on average increase their proportion in the assemblage by that ratio each sample, while those below 1 disappear; it is therefore no coincidence that exactly half the number of taxa are above and half below this value. The mean ß value is plotted alone for single observations, range for two or more values and standard deviation where three or more values are available. In the latter case, number of occurrences are plotted on the right y-axis and labelled on the main plot.

ß value ranking appears to provide a more plausible order to species resistance, similar morphologies tending to perform comparably, for example *Mastogloia elliptica* var. *dansei* and *Ma. smithii* var. *lacustris*, both *Campylodiscus* taxa and fine *Nitzschia* spp.. Again, there are some irregularities, not least the low position of taxa such as *Chaetoceros* cysts and *Campylodiscus* taxa. The raphe valves of *Cocconeis placentula* var. *lineata* and var. *euglypta* might reasonably be expected to behave similarly, as the obvious difference at the scale of gross valve structure (as seen under LM) is in the rapheless valve, but the opposite is the case. This might be reflecting the true dissolution susceptibility of the taxa, in which case it points to the importance of ultrastructure in controlling valve resistance, or, perhaps more easily, errors in the use of the raw ß value data.

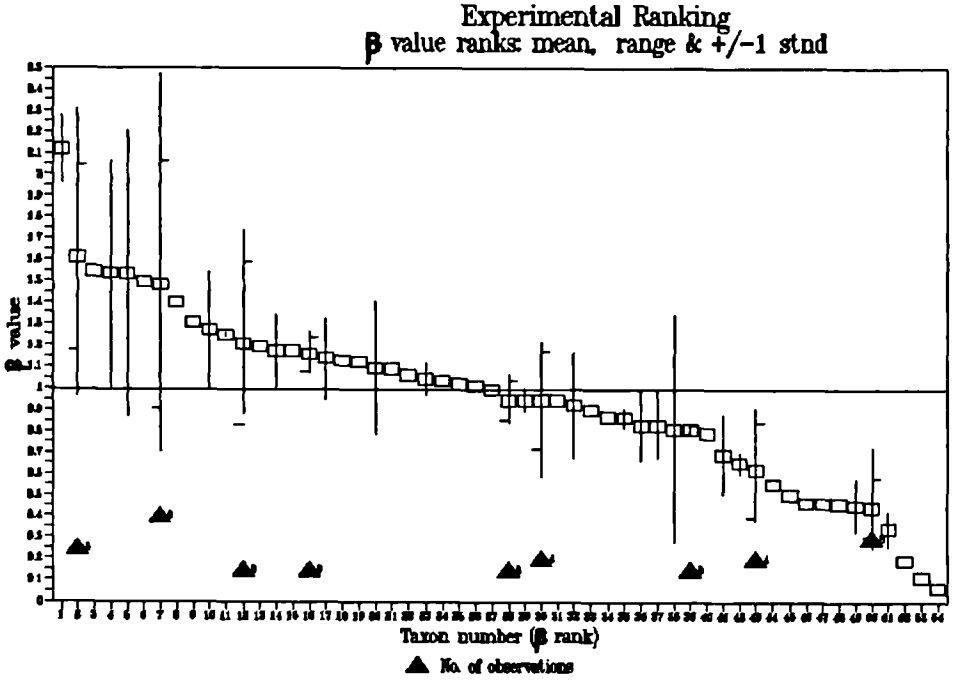
From the figure of ß values (figure 5.26), it can be seen that where a taxon appears in several assemblages, there is often a large spread of values, which are averages themselves. Quite apart from the errors of counting that are implicit in the calculation of **r** and ß values, variation in ß values may reflect dissimilar resistance to dissolution due to different sources of the same taxon. Under LM and SEM there does not appear to be any difference between valves of the same taxon from different origins, the two exceptions noted in this study being the smaller average size of *Cyclotella meneghiniana* from Elbow Lake samples to all other occurrences, and the presence of uncysted *Chaetoceros* cells from Coldwater Lake, implying that other samples were less than pristine. It is not possible to discount this hypothesis on this basis as it is the ultrastructure that is the site of dissolution and so the major source of variation in dissolution behaviour.

Nevertheless, ß values are not absolute and independent measures but depend on the

Table 5.5 - Experimental ranking (β-rank)

β-rank			
Rank	**Taxon**	**Rank**	**Taxon**
1	Mastogloia elliptica	28	Amphora pediculus
2	Navicula oblonga	29	Cyclotella meneghiniana
3	Mastogloia smithii var lacustris	30	Stephanodiscus niagarae
4	Rhopalodia gibba	31	Cymbella pusilla
5	Surirella ovalis	32	Surirella striatula
6	Amphora libyca	33	Amphora coffeaeformis
7	Epithemia turgida	34	Navicula capitata var capitata
8	Gomphonema pumilum group	35	Opephora cf olsenii
9	Fragilaria lapponica	36	Cocconeis pediculus +
10	Cocconeis placentula var lineata -	37	Cyclotella caspia
11	Cocconeis placentula var euglypta -	38	Cocconeis placentula var euglypta +
12	Aulacoseira granulata (all forms)	39	Cocconeis neothumensis -
13	Cocconeis pediculus -	40	Navicula erifuga
14	Achnanthes delicatula (all forms)	41	Brachysira aponina
15	Chaetoceros cysts	42	Nitzschia frustulum
16	Cocconeis placentula var lineata +	43	Achnanthes minutissima (all forms)
17	Rhoicosphenia curvata (all forms)	44	Diatoma moniliformis
18	Synedra fasciculata	45	Navicula halophila
19	Fragilaria construens	46	Cocconeis neothumensis +
20	Campylodiscus clypeus - large	47	Fragilaria pinnata
21	Cyclotella quillensis	48	Nitzschia aff fonticola var 1
22	Fragilaria brevistriata (all forms)	49	Nitzschia palea
23	Nitzschia amphibia	50	Nitzschia E35
24	Gomphonema olivaceum	51	Stephanodiscus minutulus
25	Anomoeoneis costata	52	Chaetoceros - no cysts
26	Campylodiscus clypeus - small	53	Cyclostephanos tholiformis
27	Gomphonema parvulum		

Figure 5.26


Experimental Ranking
β value ranks: mean, range & +/-1 stnd
β value
Taxon number (β rank)
No. of observations

assemblage context of an individual taxon, and the potential increases in proportion that a taxon could make. As an extreme example, in an assemblage in which three taxa are equally abundant at t=0, the maximum **r** value of the most robust taxon is 3, whereas the same three taxa in the proportion 1:2:3, with the most robust first, the maximum **r** value is 6. The maximum **r** value of any taxon is inversely proportional to its initial proportion in the assemblage, and as this condition varies amongst all assemblages, resultant **r** and ß values are of unequal weights in each assemblage.

Several methods to weight the ß data were attempted, including dividing ß values by the sum of **r** values over all samples in each assemblage (β') and developing another index based on the ratio of the sum of **r** values for a taxon to the sum of all **r** values for all taxa in the assemblage (renamed β'' values). All such methods were ultimately unsatisfactory and although the ranking produced had much in common with each other and the original r ranking, this was to be expected as they were all ß value derived. There could be no coherent reason why any ranking should be better than the next, even if it appeared so, as the fundamental ß values were not absolute measures of dissolution resistance and, as for the $\mathbf{a_1}$ and $\mathbf{a_2}$ data, "improvements" would probably only be coincidental to the somewhat arbitrary transformations applied to the data.

5.2.1.3 Comparison of ranking methods

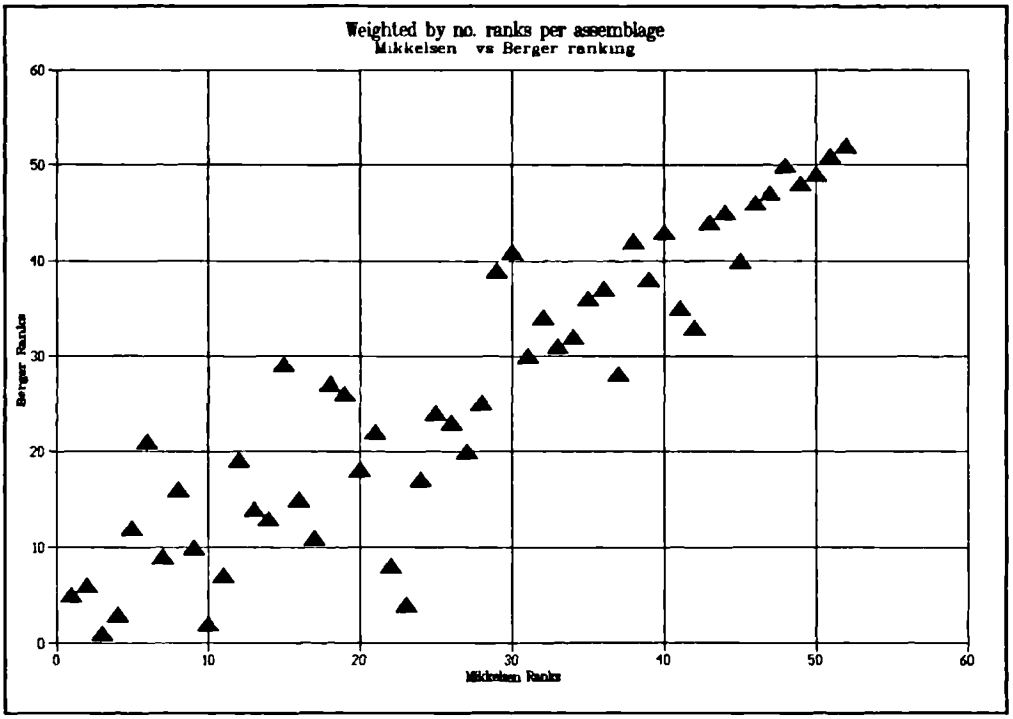
As a test of the objectivity of ranks produced using Mikkelsen's method, species were also ranked using Berger's index (1968) on the same data. This index (I_B) also compares taxa through paired samples, as follows;

$$I_B = \frac{(m-2)!\ 2!}{m!} \cdot \sum_{i=1}^{b} \frac{(y_i - y_k)}{(y_i + y_k)} \qquad (3)$$

where **m** is the number of observations of the proportion of a taxon **y** compared for all pairs of samples.

Taxon percentages are compared from later to earlier samples (deeper to shallower samples in the original marine context), so that positive values result if proportions increase with dissolution, for all samples. Within each assemblage, calculations are made for all such pairings, which unlike Mikkelsen's index does not use the initial sample as the comparison for all other samples. The sum is calculated for all taxa for all samples within an assemblage, and the values averaged for taxa appearing in more than one assemblage. Figure 5.27 compares the unadjusted ranks derived under both systems which give broadly similar results. Dissolution

Figure 5.27


Weighted by no. ranks per assemblage
Mikkelsen vs Berger ranking
Berger Ranks
Mikkelsen Ranks
0
10
20
30
40
50
60

ranking was explored further using Mikkelsen's index, as it is computationally simpler and performs similarly to Berger's index.

5.2.1.4 *A*-ranking

If dissolution behaviour is an absolute property of taxa, then the **r** values between taxa should exhibit a systematic relationship. The relationships between **r** values of several taxa found in the same assemblages were analysed. Figures 5.28 & 5.29 show this relationship between the taxon with the most observations, *Amphora libyca*, and *Navicula oblonga* (figure 5.28) and *Nitzschia palea* (figure 5.29). The nature of the correlation differs between the taxa, linear and positive with *Navicula oblonga* (r^2=0.513, r=+0.716, 28 degrees of freedom, p=0.005) and exponential decline with *Nitzschia palea*, the difference in part associated with the complete disappearance of *Ni. palea* at large **r** values of *Am. libyca* at later stages of dissolution. Linear correlation does appear to hold if zero *Ni. palea* **r** values are ignored (r^2=0.418, r=-0.646, 16 degrees of freedom, p=0.005) and appears to hold in other cases where both **r** values are increasing, comparing robust taxa.

This systematic behaviour transcends differences in source of taxa as well, suggesting that the intraspecific variation is less important than between taxa, and supporting the idea of a taxonomically-based system of dissolution which has some validity regionally and possibly beyond. Factors of biogeography and environmental conditions of diatom growth are undoubtedly important, and some variation in dissolution behaviour can thereby be explained, but appear of secondary importance here.

By standardising ß values, taxa can be directly compared, and as *Amphora libyca* appears in 8 out of the 11 assemblages, this taxon was chosen as the standard to which all other taxa could be compared. The ß values of all taxa were divided by the ß value of *Amphora libyca* for each assemblage, and these new values averaged across all occurrences to produce a final index (the *Amphora* or ***A***-index). For assemblages **C** and **F**, the average ***A*** value of *Nitzschia palea* from assemblages ***A***, **B**, **D** and **E** was taken as the adjustment factor and the ß values reduced accordingly. The ß values of *Nitzschia palea* in these two cases are about 0.4, and lie within the region of linear correlation with *Amphora libyca* (figure 5.29). Assemblage I was adjusted by taking the only taxon found in another sample, *Surirella ovalis*, as the standard for the assemblage, which is subject to some uncertainty as there is only one observation linking this assemblage to the others (*Su. ovalis* from assemblage D).

Although not ideal, the ***A*** index produced does have fewer disadvantages than any of the other systems, and so the ranking derived from it is considered the best approximation to the reality

Figure 5.28

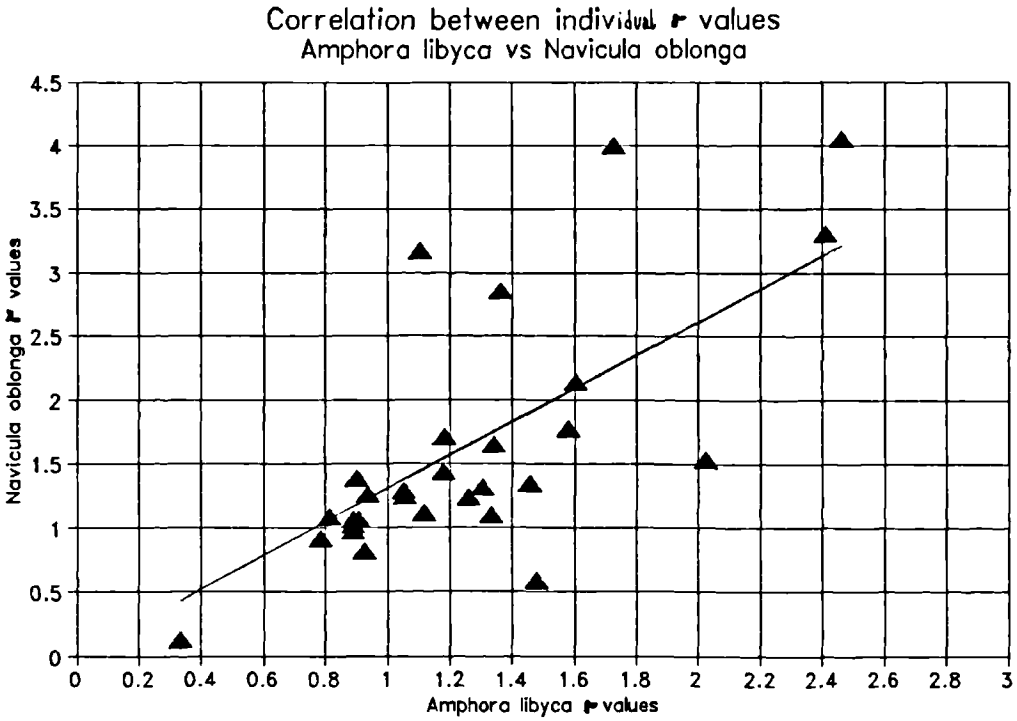
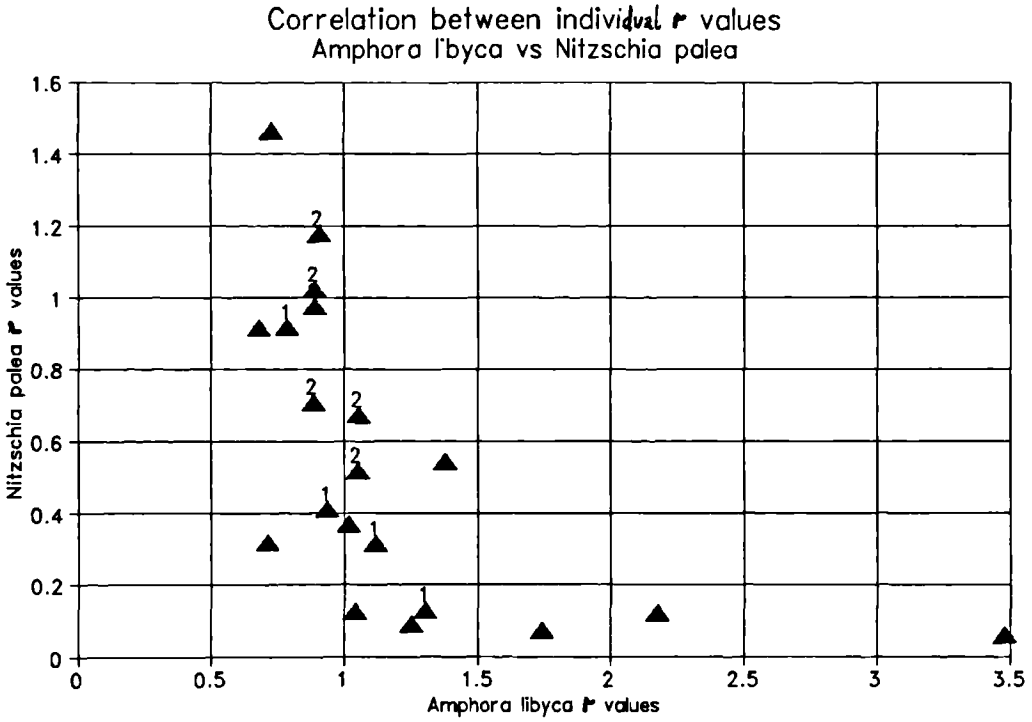


Figure 5.29



as the percentage data will allow. The values of ***A*** for taxa, and the resultant ranking, is shown in figure 5.30, in the same format as figure 5.26, and table 5.6. As before, taxon rank relates to the order in the associated table, most resistant (largest ***A*** values) at the top. As before, many related taxa (genetically and morphologically) are closely ranked in resistance, with valves of all raphid *Cocconeis* ranking below their rapheless counterparts. The higher positions of such taxa as *Campylodiscus* spp. and *Chaetoceros* cysts agrees much more with field and casual observations (J. Reed pers. comm. 1993, Flower 1993) and in general taxa thought of as fragile do appear lower down the order. There are still some surprises, such as the high position of *Stephanodiscus niagarae* (2nd), *Amphora coffeaeformis* (18th) and *Brachysira aponina* (28th) and low positions of *Cyclotella quillensis* (19th) and *Cy. meneghiniana* (31st), which suggest that the order is not perfect, but perhaps as good as can be expected within the limits of the original data. For example, *Cyclotella quillensis* and *C. caspia*, included in experiment 2 consisted of both well preserved and some dissolved valves, which could not be separated from the original natural samples. For this reason, if such rankings are to be used, the 54 ranks could be grouped into perhaps 8 or 10 categories of similar behaviour, to smooth out such anomalies.

5.2.2 Using absolute abundance changes

For many taxa, it was possible to follow absolute population decline over time. The rate of decline can be used as a means of ranking taxa, as it can be hypothesised that more resistant forms will disappear more slowly than fragile taxa. As suggested before, dissolution rate of solid silica will vary with specific surface area and dissolved silica concentration, hence it will differ over time within and between assemblages. Within an assemblage, all valves will have experienced the same dissolution rate at any time, and the slope of population decline can be used to rank the taxa within the assemblage. In the same way as with ß values, taxon population decline can be standardised according to common taxa, either in terms of the rate of population loss or time taken for a fixed proportion to dissolve (perhaps the "dissolution half-life", Glover 1982). Population calculations rely on the ratio of percentage occurrence in initial and subsequent samples, and so incorporate **r** values, and therefore are not a truly independent means of ranking taxa.

5.3 Counting using dissolution stages

5.3.1 Developing dissolution indices

Diatom dissolution behaviour is in part explained by an analysis of percentage data, but has little diagnostic value without reference to the condition of valves found in a sample. In

Figure 5.30

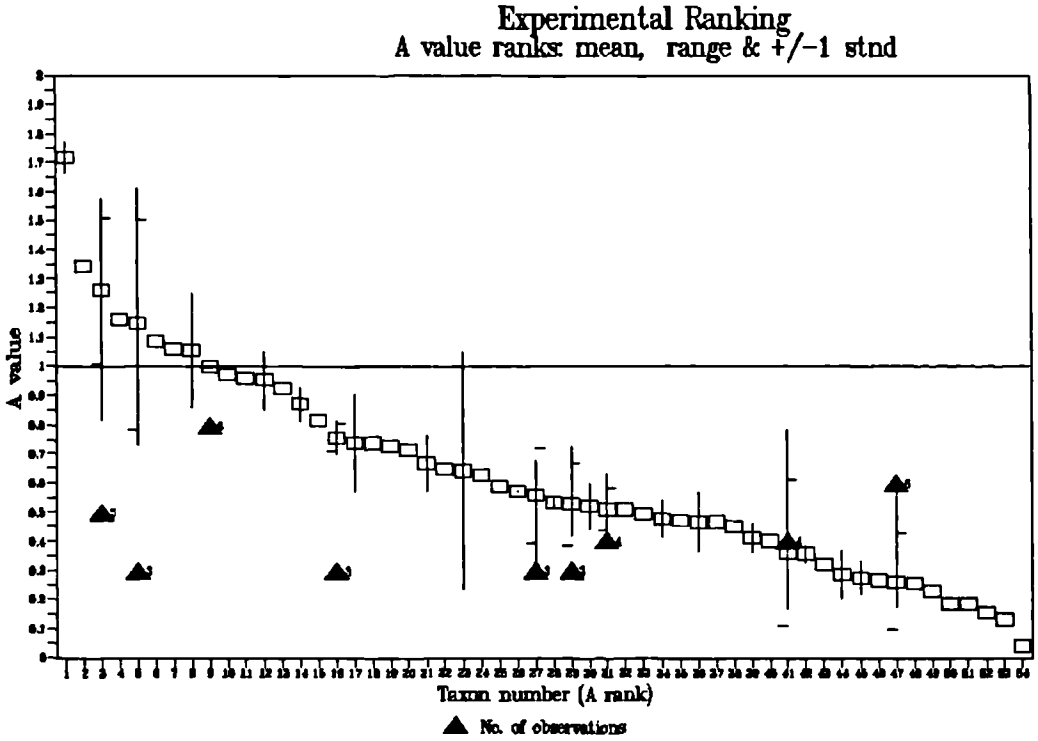

Experimental Ranking
A value ranks: mean, range & +/-1 stnd
A value
Taxon number (A rank)
No. of observations

Table 5.6 - Experimental ranking (*A*-rank)

***A*-rank**			
Rank	**Taxon**	**Rank**	**Taxon**
1	Mastogloia elliptica	28	Gomphonema parvulum
2	Stephanodiscus niagarae	29	Cocconeis placentula var lineata +
3	Navicula oblonga	30	Cyclotella meneghiniana
4	Campylodiscus clypeus - large	31	Rhoicosphenia curvata (all forms)
5	Chaetoceros cysts	32	Achnanthes delicatula (all forms)
6	Anomoeoneis costata	33	Opephora cf olsenii
7	Campylodiscus clypeus - small	34	Gomphonema olivaceum
8	Fragilaria lapponica	35	Fragilaria construens
9	Amphora libyca	36	Nitzschia amphibia
10	Synedra fasciculata	37	Fragilaria brevistriata (all forms)
11	Surirella striatula	38	Amphora pediculus
12	Cocconeis pediculus -	39	Navicula halophila
13	Surirella ovalis	40	Nitzschia frustulum
14	Rhopalodia gibba	41	Navicula capitata var capitata
15	Aulacoseira granulata (all forms)	42	Cocconeis neothumensis -
16	Cocconeis placentula var euglypta -	43	Navicula erifuga
17	Cymbella pusilla	44	Nitzschia E35
18	Amphora coffeaeformis	45	Nitzschia aff fonticola var 1
19	Cyclotella quillensis	46	Nitzschia palea
20	Mastogloia smithii var lacustris	47	Achnanthes minutissima (all forms)
21	Cocconeis pediculus +	48	Diatoma moniliformis
22	Epithemia turgida	49	Cocconeis neothumensis +
23	Cyclotella caspia	50	Fragilaria pinnata
24	Gomphonema pumilum group	51	Chaetoceros - no cysts
25	Cocconeis placentula var lineata -	52	Stephanodiscus minutulus
26	Cocconeis placentula var euglypta +	53	Cyclostephanos tholiformis
27	Brachysira aponina		

particular, the validity of the experimental approach to ranking taxa on resistance to dissolution assumes that valves are in the same, pristine, condition; that is, the comparison is of like with like. Both these points can be addressed by considering how the assemblage as a whole, and individual taxa, degrade during the dissolution process.

All valves counted in all samples were allocated into a dissolution category, and although a dissolution sequence had not been identified for all valves encountered, all significant taxa in each assemblage (generally those appearing at above 3% in any sample) were included. Rare taxa that were encountered were classed according to stage systems of morphologically similar taxa for which sequences had been established (*e.g. Surirella peisonis* sequence followed *Su. ovalis*, *Gomphonema* species on the basis of *G. olivaceum* and *G. parvulum*).

In general it was possible to identify more stages for larger valves, which had distinct valve segments with consistent differences in specific surface area. Structures with high surface area to volume ratios (under LM and SEM), such as pore fields and areas with high striae density, tended to dissolve preferentially to those with low ratios, such as central areas. Raphes often acted as lines of relative susceptibility in resistant apical zones, commonly leading to valve break up at a critical dissolution threshold. As the final criterion for counting was an unambiguous association of a remnant to a single valve, dissolution effectively reduces the countable population before all silica has dissolved, depending on the taxon.

Indices of sample preservation discussed in the literature that are based on microfossil characteristics have traditionally depended on the proportion of resistant species in the assemblage. In situations where initial sample composition can be expected to be similar, this approach has ample justification and validity, for instance in marine surface sediment studies (*e.g.* Ruddiman & Heezan 1967, Berger 1968, McIntyre & McIntyre 1971, Peterson & Prell 1973, Thunnell 1976, Shemesh *et al.* 1989). This procedure is more open to question where the assumption of initial sample homogeneity is unclear. Over a larger gradient of environmental change, in time or space, differences in the death assemblage relate to changes in the live environment as well as to taphonomy.

Relatively few published studies have been made on microfossil preservation and morphological changes. McIntyre & McIntyre (1971) give a sequence of degradation for several heterococcoliths from deep-sea core tops and experiments using ultrasonic vibration, to rank taxa according to physical resistance to destruction, and Beyens & Denys (1982) discussed diatom valve fragmentation. More recently, Mayer *et al.* (1991), Barker (1992), Flower (1993) and Barker (1994) have demonstrated stages in the dissolution process for several taxa. Preservation indices have been developed for specific diatom taxa in soda lakes of East Africa

(Barker 1990, 1992) and freshwater Lake Baikal (Flower & Likhoshway, 1993), focusing on changes in diatom morphology from dissolution effects.

Barker's index (1990) uses the ratio of dissolved to whole valves of *Cyclotella meneghiniana*, common in the samples and robust within the assemblages, to classify sample preservation. Flower & Likhoshway (1993) developed a diatom dissolution index ("Flower's DDI") to compare preservation of modern (sediment trap) and recent (surface sediment) samples, based on the ratio of stage 1 (pristine) valves to all valves of three common taxa (*Aulacoseira baicalensis*, *Cyclotella minuta* and *Cy. ornata*). Although not formalised as an index, Mayer *et al.* (1991) divided the progressive dissolution of the marine diatom *Odontella aurita* into a sequence of three stages.

All *Cyclotella* species involved in the dissolution experiments (*Cy. caspia*, *Cy. meneghiniana* and *Cy. quillensis*) had four dissolution stages, and as no taxon was present in all samples, neither index could be used directly. Instead, several indices were investigated based on different transformations of the stage-counted data. Flower's DDI, applied to all taxa in a sample, provides a uniform index varying between 0 and 1 (perfect preservation), irrespective of the morphological types in a sample (and the potential for valves to develop high stage dissolution profiles). This is both the advantage and drawback of this index; it allows for comparison between any samples, but is not sensitive to highly dissolved assemblages where changes in stages 2-4 may be important. In extreme cases, with no stage 1 valves, samples are equally treated as badly preserved (DDI=0).

Five other indices were considered, treating the stage categories as weighting factors in various forms, of which two were applied to the data, together with Flower's DDI. These other indices are referred to as the weighted index (W), and the square weight index (W^2), treating the total number of valves for each taxon as the weight. These indices can be represented by the following notation:

$$DDI_x = \frac{x_1}{\sum_{s=1}^{4} x_s} \qquad (4)$$

$$W_x = \frac{\sum_{s=1}^{4} x_s . s}{\sum_{s=1}^{4} x_s} \quad (5)$$

$$W_x^2 = \frac{\sum_{s=1}^{4} x_s . s^2}{\sum_{s=1}^{4} x_s} \quad (6)$$

where

x_s is the number of valves of taxon **x** counted at stage **s**

s is the stage number (an integer between 1 and 4)

The sum is made for all values of **s** and x_s for each taxon, and can be applied to all taxa to give sample indices. **W** and W^2 vary between 1 and s_{max} or s^2_{max} (the number of stages recognised in a taxon dissolution sequence) respectively. These indices are only directly comparable for taxa with the same number of dissolution stages, and in the case of assemblages, they will only be comparable if the initial proportions of taxa with maximum stages 2, 3 and 4 are the same. Any single index cannot cover all situations, and each performs optimally under different conditions. The use of all three indices together allows for all dissolution situations to be covered, as information lost using one index can be captured with the others. For taxa with only 2 stages, such as most *Nitzschia* spp. considered here, Flower's DDI mirrors **W** (varying between 1-2); **W** and W^2 only come into their own with stage 3 and 4 assemblages.

Appendix 2 contains the diagrams charting the development of the three dissolution indices for each important taxon from all 11 assemblages, either against population decline or time (sample number). Population changes are only plotted for those taxa with initial percentages over about 5% (44 examples), to reduce errors from counting, as population values depend crucially on initial values, below which dissolution indices are plotted against sample number (53 examples). Time increases from right to left (as population declines) in the former cases, and from left to right (as sample number increases) in the latter.

Rather than consider each plot separately, many of the main points can be made from the figures of total sample population against dissolution indices for each assemblage (figures 5.31-5.41) and selected species diagrams (figures 5.42-5.46).

5.3.2 Assemblage population and dissolution indices (figures 5.31-5.41)

Figure 5.31

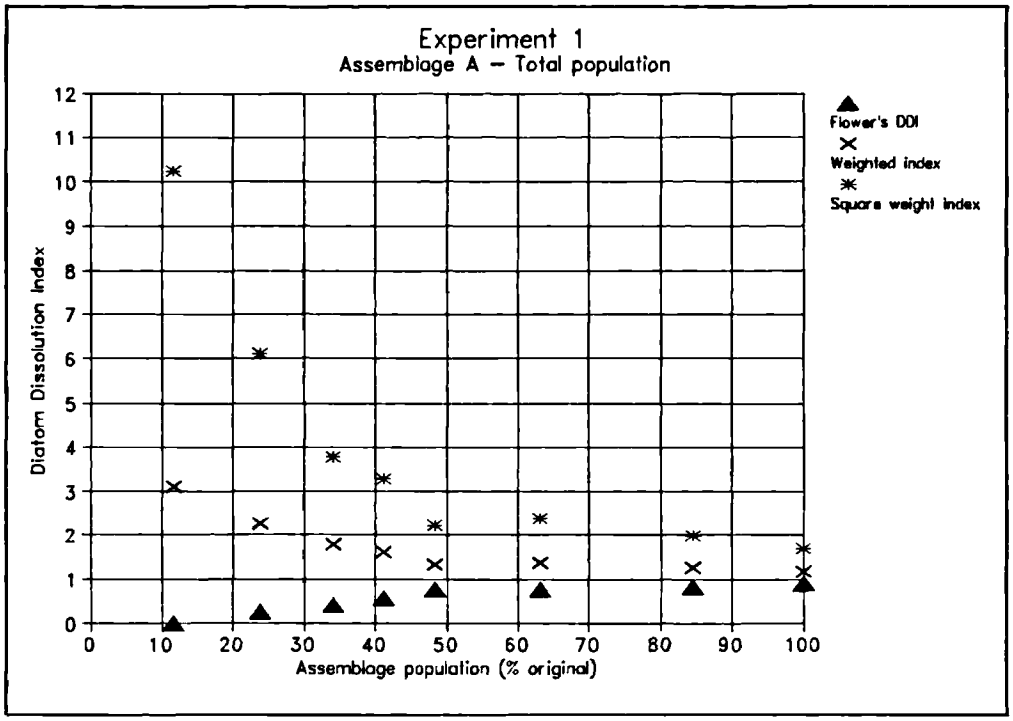


Figure 5.32

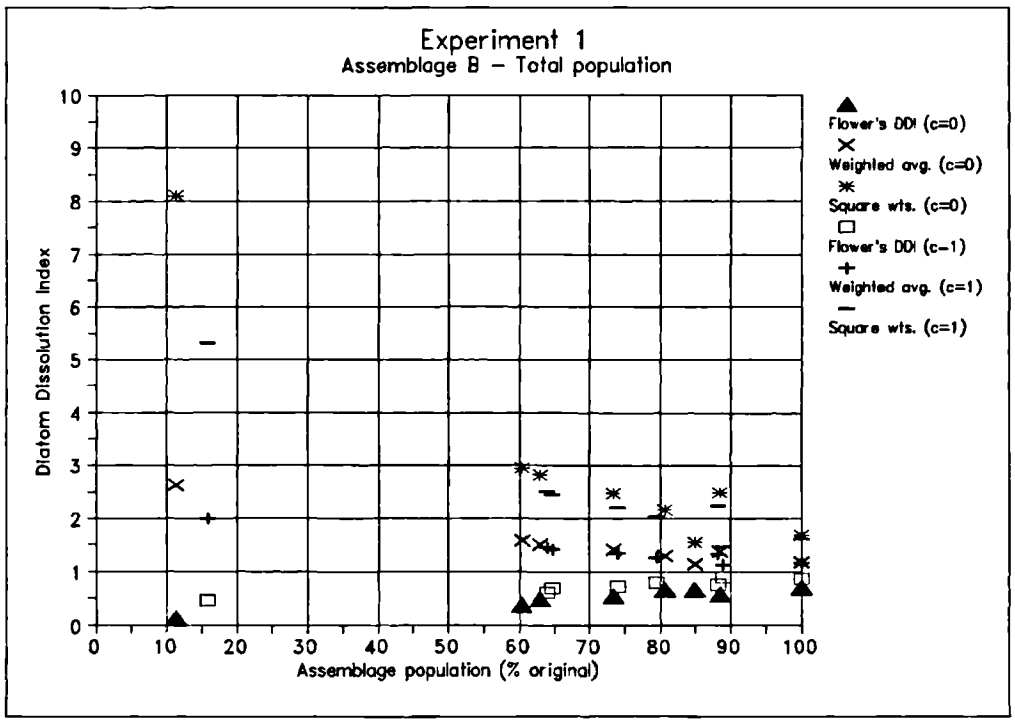


Figure 5.33

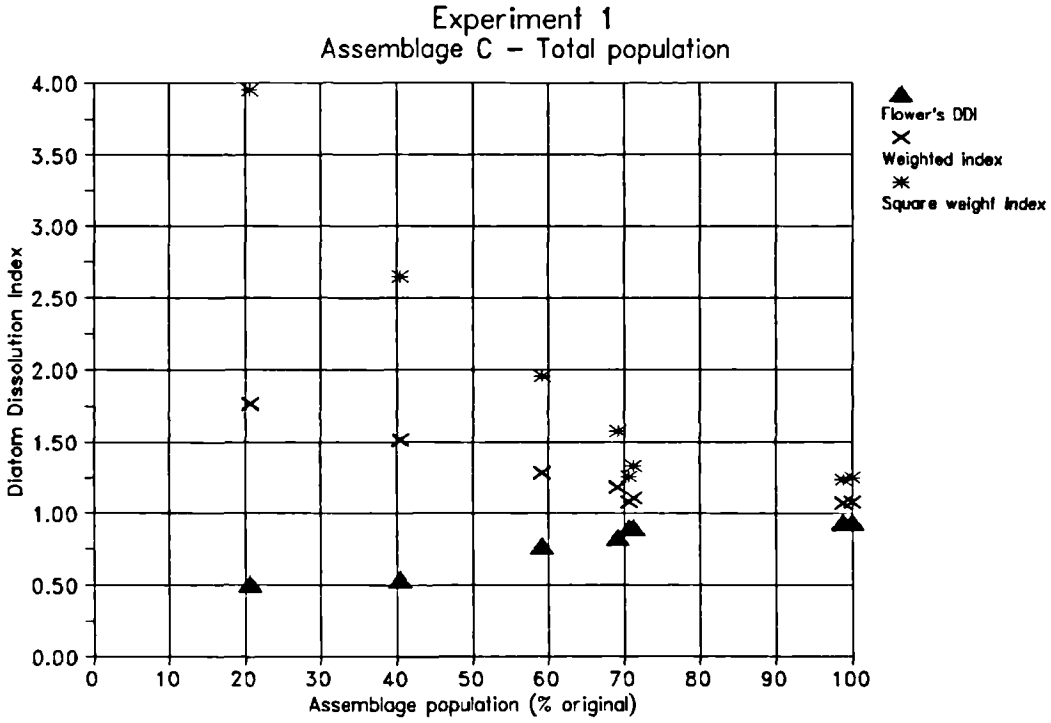


Figure 5.34

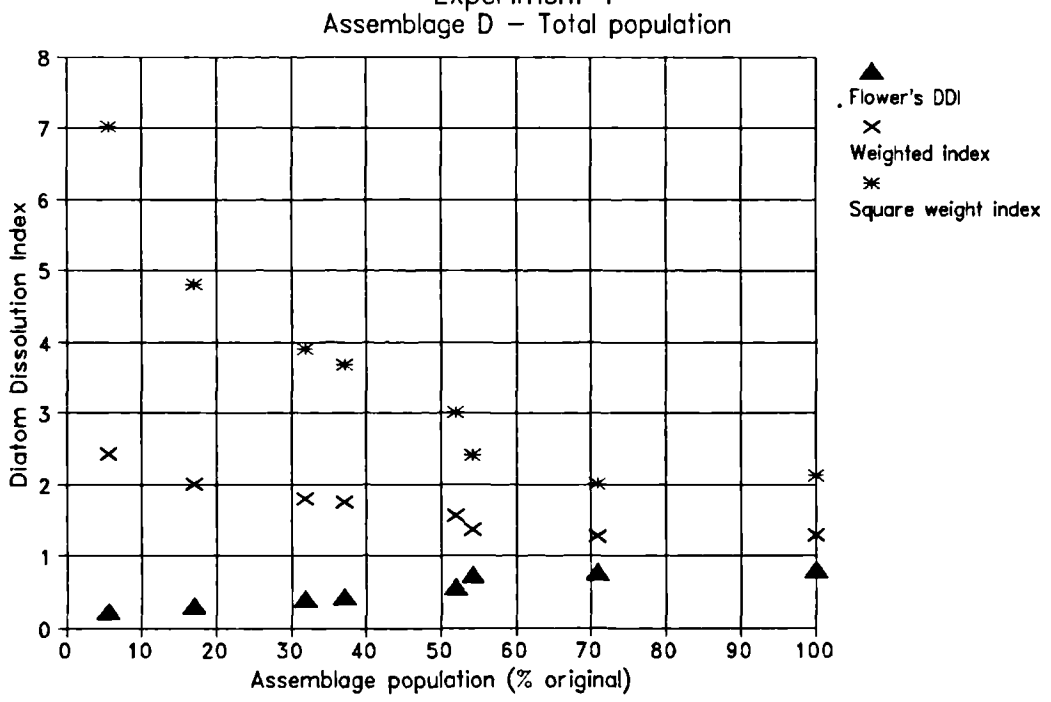


Figure 5.35

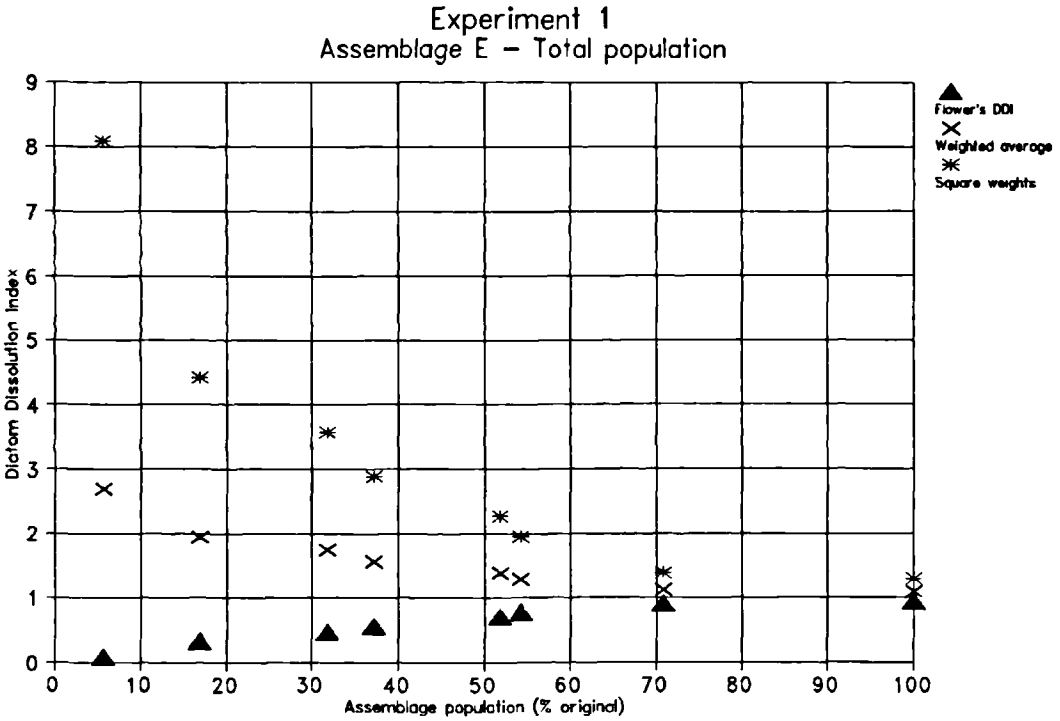


Figure 5.36

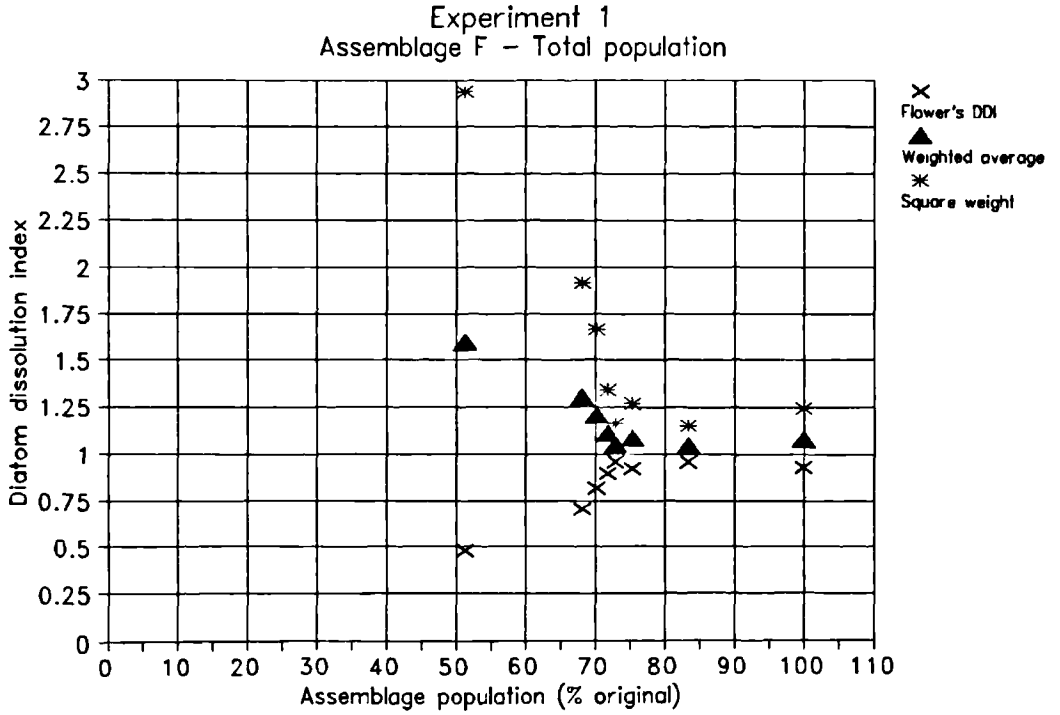


Figure 5.37

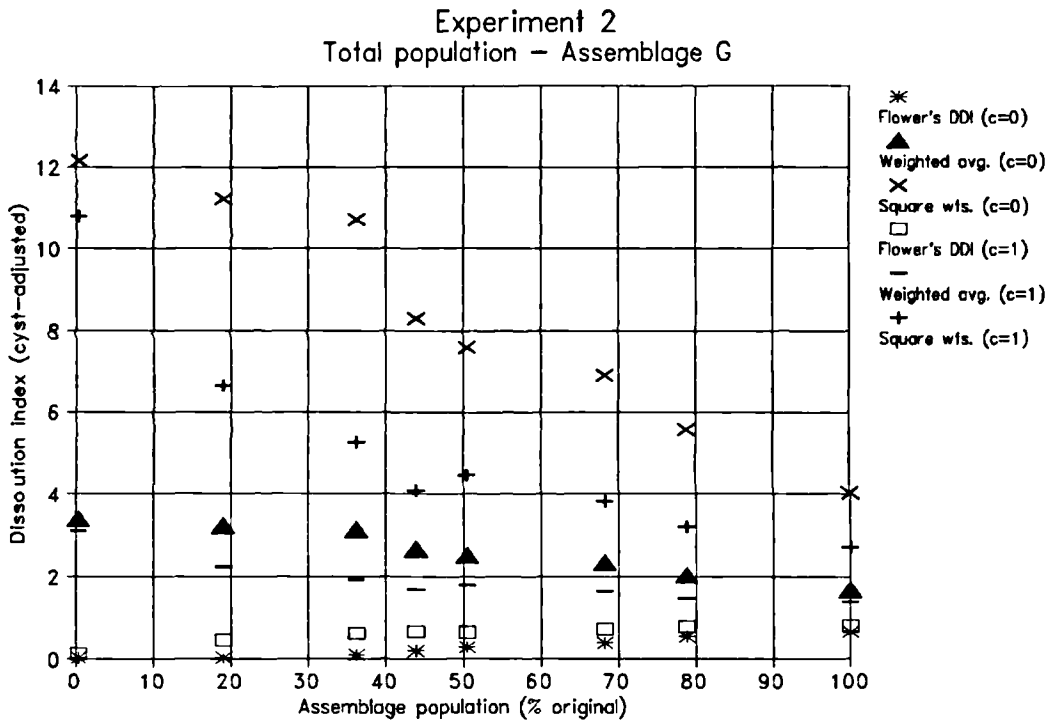


Figure 5.38

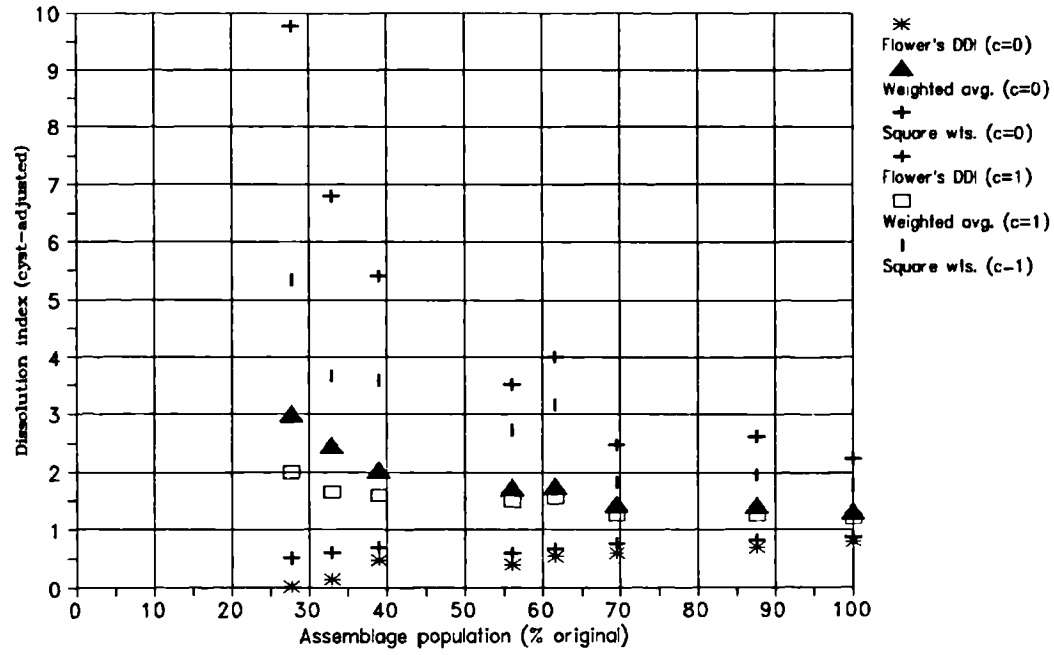


Figure 5.39

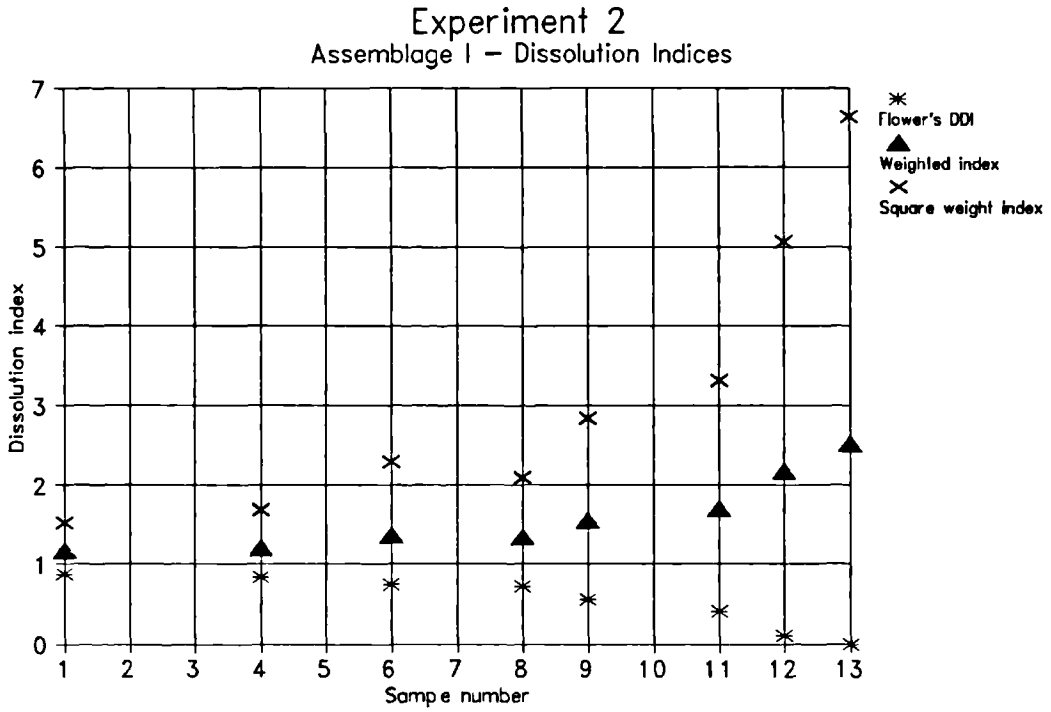


Figure 5.40

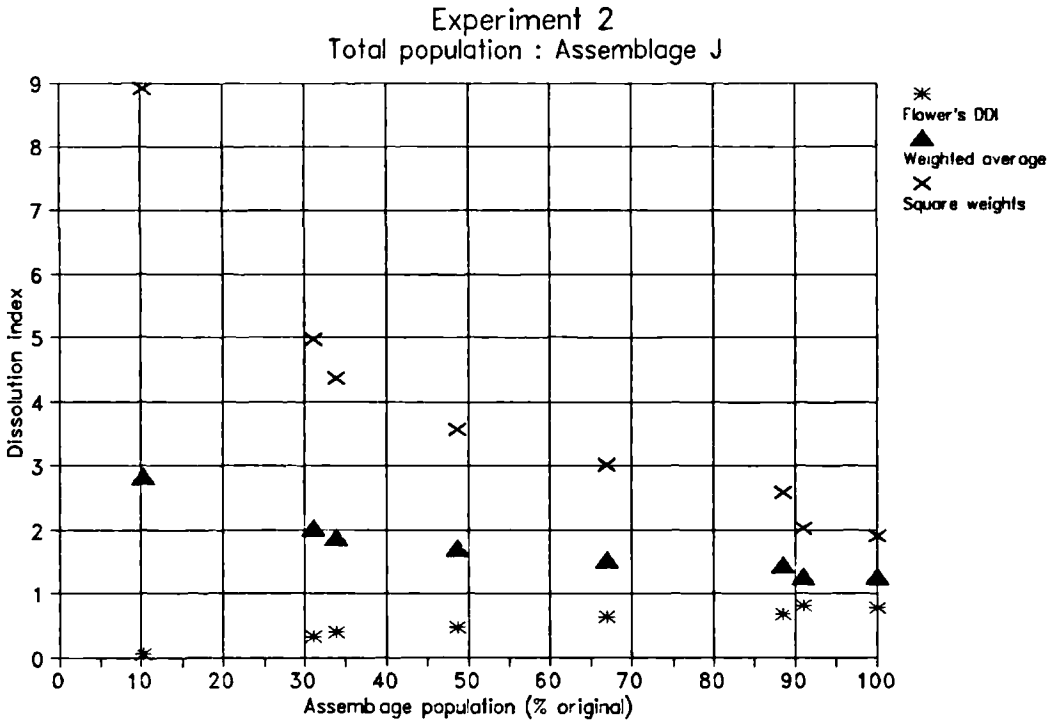


Figure 5.41

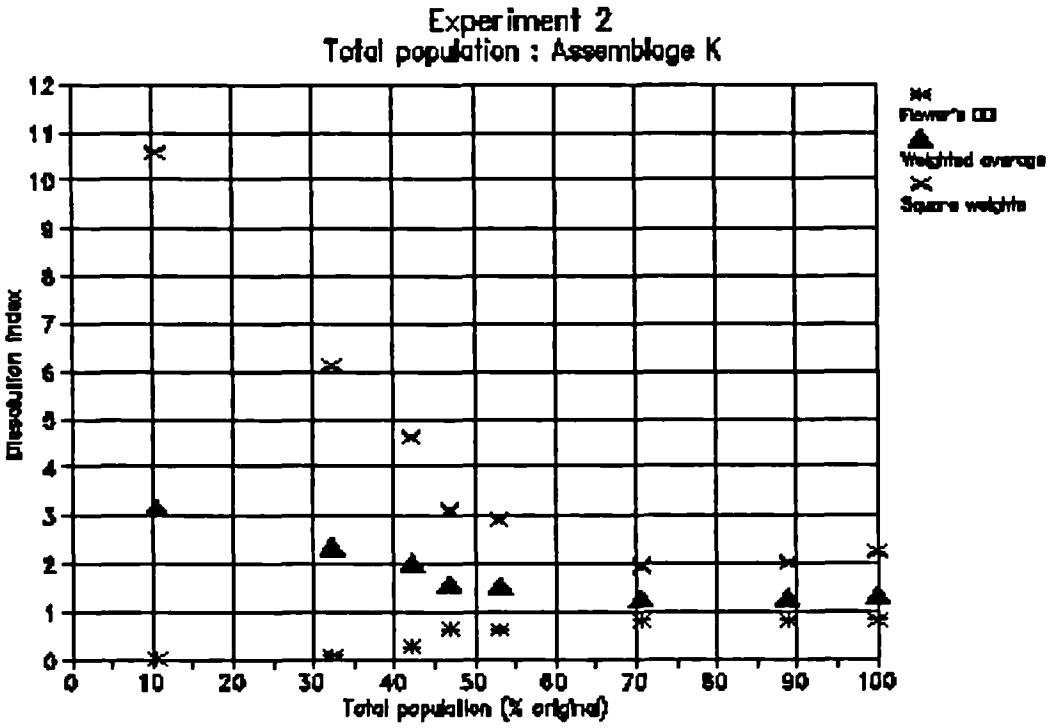

Experiment 2
Total population : Assemblage K
Dispersion index
Total population (% original)
Weighted average
Square weights

Figure 5.42

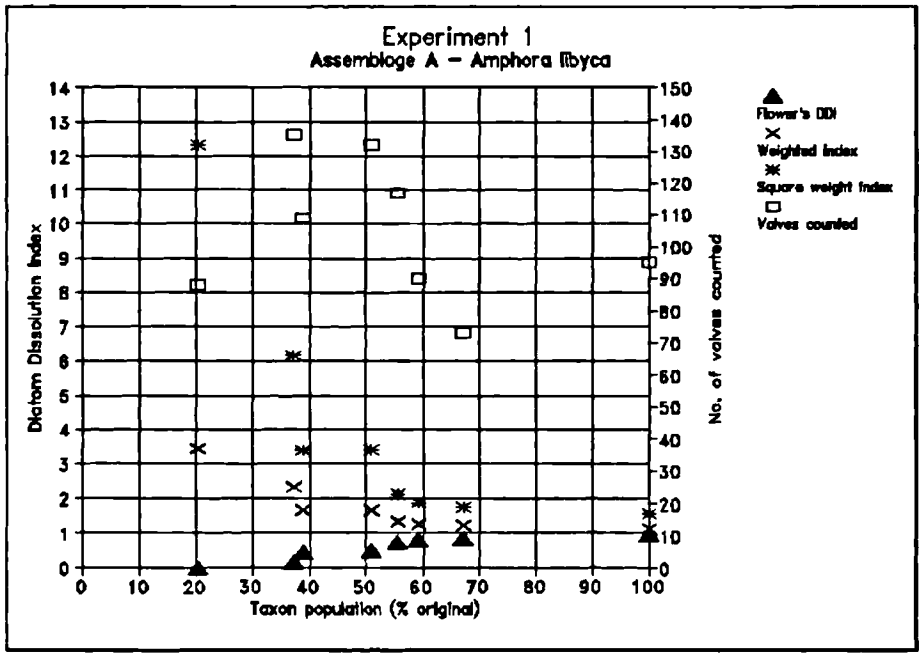


Figure 5.43

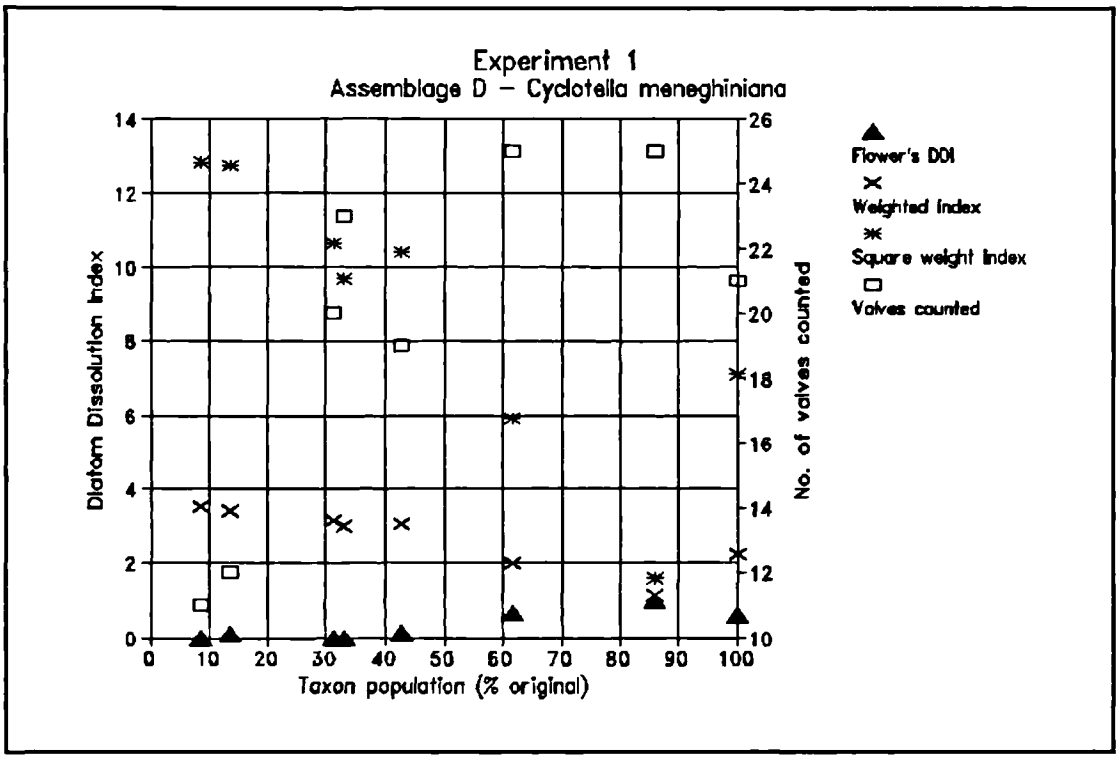


Figure 5.44

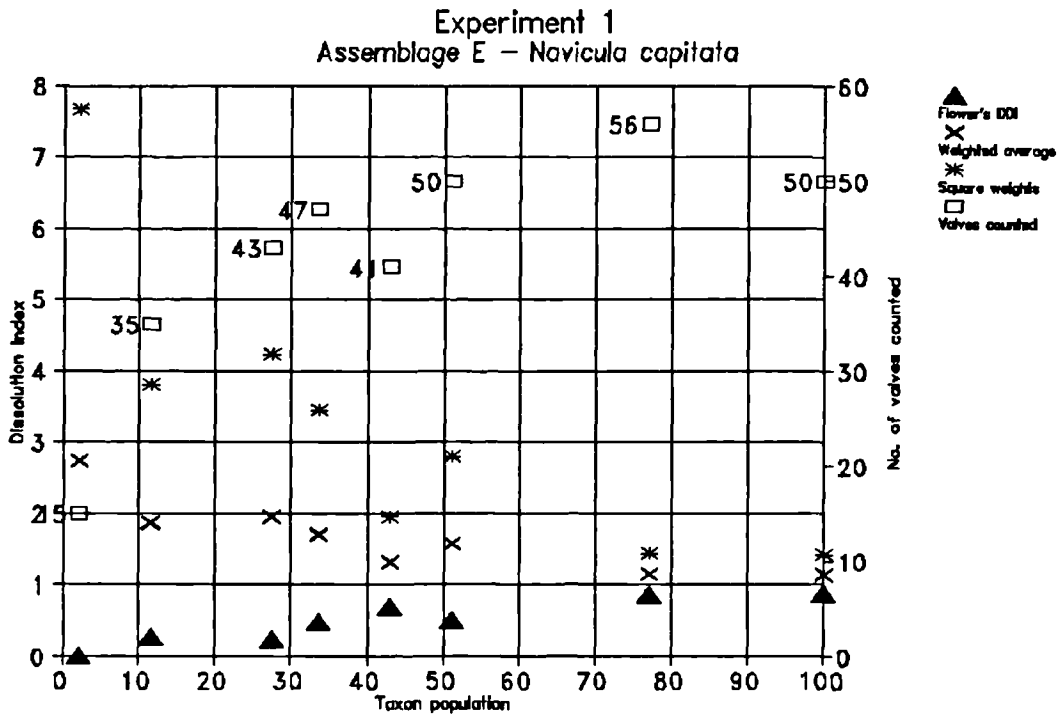


Figure 5.45

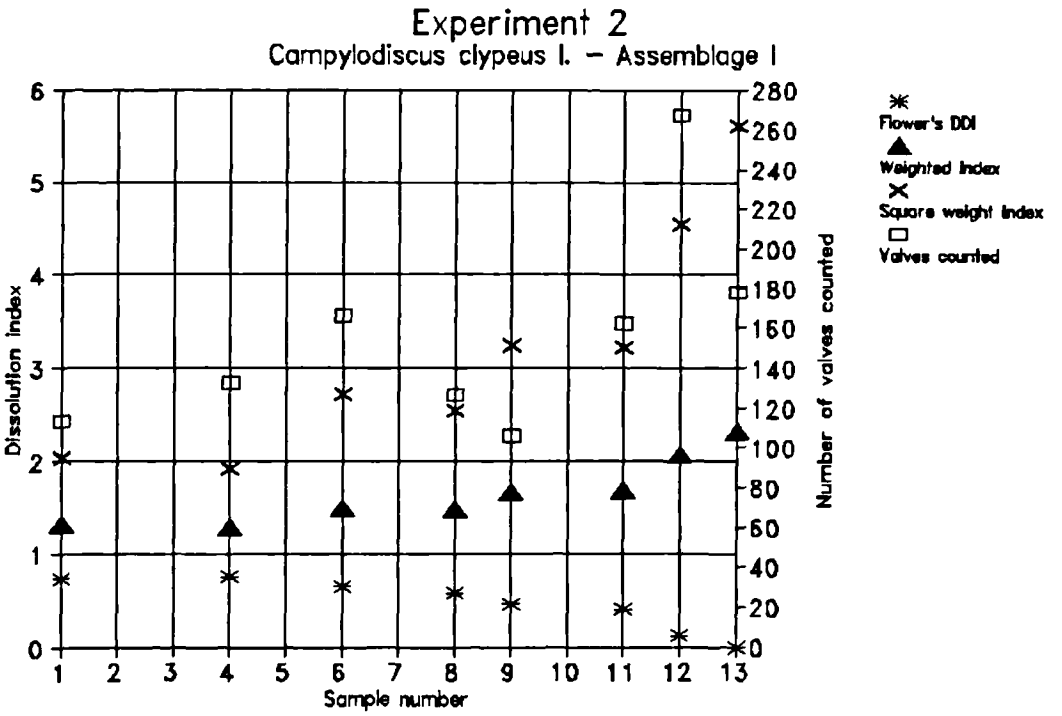
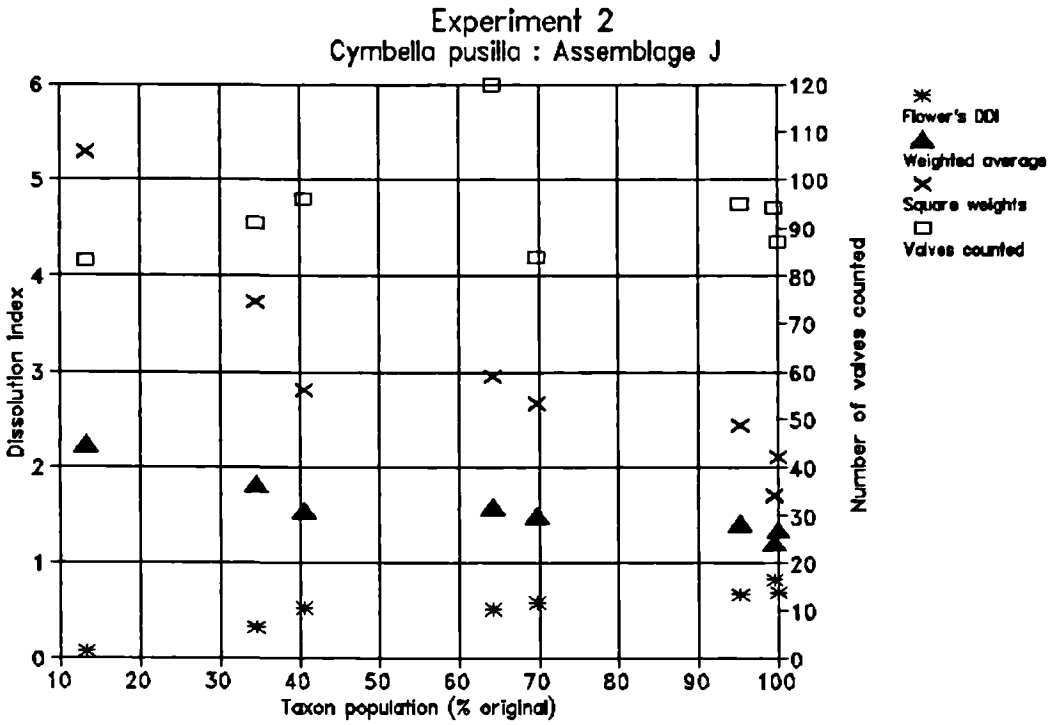


Figure 5.46


Experiment 2
Cymbella pusilla : Assemblage J
Dissolution Index
Number of valves counted
Taxon population (% original)
Flower's DDI
Weighted average
Square weights
Valves counted

All assemblages start with index values indicative of good preservation, which tend to show little change (even with the exaggeration of higher stages using W^2) despite population losses of between 20-50%. After this initial period, a threshold appears to be crossed with all indices showing a steady increase in dissolution as population declines. This trend is repeated for many individual taxa (Appendix 2), implying that a proportion of valves even from an apparently fresh assemblage may be particularly sensitive to dissolution, particularly as solid silica dissolution rates are greatest in the earliest phase when dissolved silica levels are low.

Assemblages D, F and K, and some individual taxa, show an initial improvement in dissolution indices. This seemingly bizarre situation is possible as valves in advanced stages of dissolution disappear while well-preserved valves remain in stage 1, suggesting the variation in initial dissolution states and the different residence times of stages.

5.3.3 Species population and dissolution indices (figures 5.42-5.46)

Stage counting is most useful for taxa that can be split into 3 or 4 stages. Figures 5.42-5.46 show the experimental results for *Amphora libyca* (assemblage A), *Cyclotella meneghiniana* (D), *Navicula capitata* (E), *Campylodiscus clypeus* (I) and *Cymbella pusilla* (J). Dissolution indices tend to fall significantly only when 30-40% of the valves have disappeared, after sample 6 for *C. clypeus*. *Cyclotella meneghiniana* valves from assemblage D appear to improve in preservation state initially (as noted above for some assemblages), which may be due to rapid and selective removal of poorly preserved valves. Confidence in the accuracy of dissolution indices can be expected to improve with larger valve counts, although this may be less of a problem for taxa, such as *Cyclotella* species, with unambiguous stages and less chance of analytical diagnosis. Mayer *et al.* (1991) counted 50 valves for dissolution studies of samples, and although counting error cannot be ruled out as an explanation for the dissolution behaviour of *Cyclotella meneghiniana*, the trend is consistent for all later samples with very similar valves counted.

Certain taxa cannot be adequately or usefully analysed by stage counting, which shows little relationship to population change, such as *Cocconeis placentula* var. *euglypta* - in assemblage B, *Co. placentula* var *lineata* + & - in assemblage F and *Chaetoceros* cysts (see Appendix 2). *Chaetoceros* cysts could not be systematically distinguished into a distinct dissolution progression, by apparent silica thickness under LM, morphological integrity or by presence or absence of setae (Appendix 1). For such a taxon, where dissolution stage counting is inapplicable, the inclusion of these valves in the sample count may bias estimated sample dissolution towards apparent better preservation, if all *Chaetoceros* valves are considered stage 1. Sample dissolution indices were recalculated for assemblages G and H, ignoring

Chaetoceros valves in both population and dissolution index calculations. Trends in dissolution are similar including all valves, but initial sample indices are noticeably lower. The difference between the indices is reduced as *Chaetoceros* cysts are dissolved from the assemblage.

5.3.4 Summary

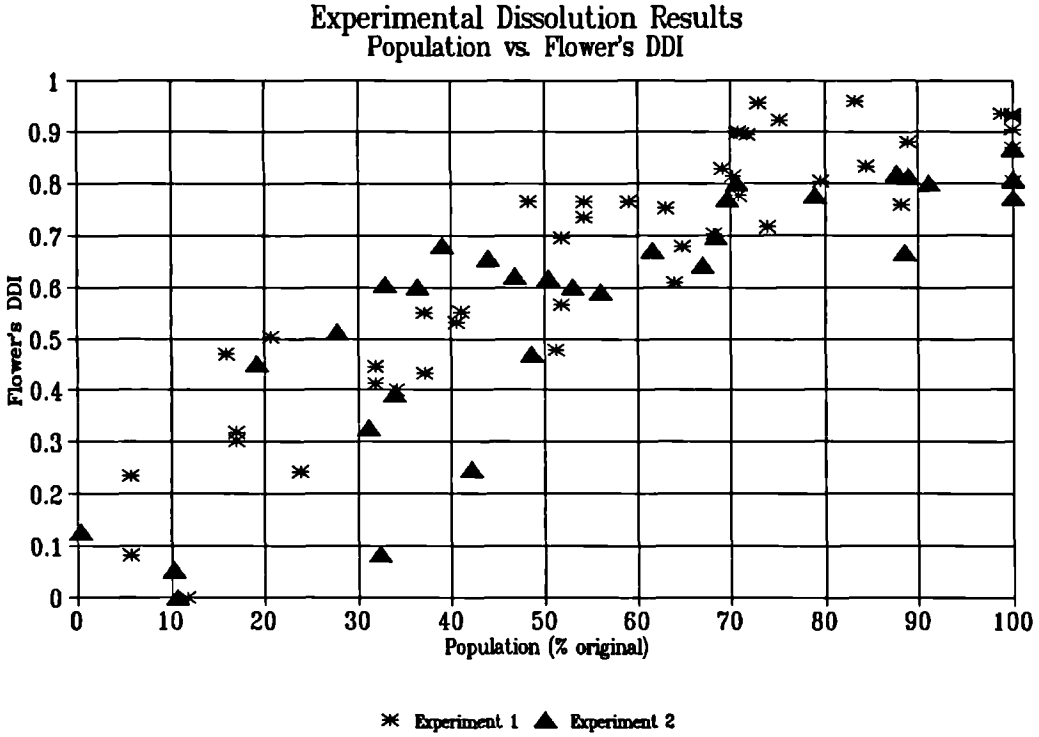
Valves can be expected to vary in dissolution parameters as well as other physical characters, affecting specific surface area. Live collections may contain senescent or dead cells, which might have started to dissolve *in situ*, although few valves may appear below stage 1 in the initial sample. Ultimately this may reflect on the residence time of valves in each stage, which implies that stage 1 tends to be the most long-lived condition for a valve. Once dissolution progresses to the point where it can be discerned under LM examination, further degradation is relatively rapid.

5.3.5 Valve abundance and dissolution indices

The maximum values of **W** and $\mathbf{W^2}$ vary among assemblages as the taxa in each differ in maximum stage. Using Flower's DDI, all assemblages can be compared more easily, as initial DDI values are approximately the same. Assemblage DDI values are plotted against population decline for the ten assemblages for which this is possible (figure 5.47). Despite great taxonomic variety represented by the assemblages, there is a strong correlation between dissolution index and population loss. Important information on diatom abundance may be recoverable from the condition (and composition) of valves left.

Dissolution experiments demonstrate that resistance to dissolution varies in a repeatable, and predictable, fashion among diatom taxa, which is systematically related to dissolution parameters. The degree to which multivariate statistical techniques can exploit this systematic relationship between dissolution parameters and valve robustness in quantitative predictions is explored in Chapter 6. The implications for environmental reconstructions incorporating differential taxon susceptibility to dissolution are tested on the Northern Great Plains salinity transfer function in Chapter 7.

Figure 5.47


Experimental Dissolution Results
Population vs. Flower's DDI
Flower's DDI
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
Population (% original)
Experiment 1
Experiment 2

Chapter 6
Prediction of dissolution parameters

6.1 Introduction

Data from dissolution experiments can be applied to preservation problems encountered in sediments along a continuum from qualitative description to quantitative analysis. Ranks of relative susceptibility can be used to provide indices of sample dissolution, based on the presence or absence of taxa from each rank group, or in a weighted form (*e.g.* Ruddiman & Heezen 1967, Berger 1968, Parker & Berger 1971, Johnson 1974, Thunell 1976, Adelseck 1978, Mikkelsen 1980, Peterson & Prell 1985, Shemesh *et al.* 1989). The use of dissolution stages may provide some refinement of this technique, although as pointed out in Chapter 5 the index by itself may not indicate the "absolute" dissolution state of a sample without reference to the constituent taxa (but see Adelseck 1978). Dissimilar samples may therefore not be directly comparable and without calibration of the indices to actual assemblage changes only dissolution trends may be highlighted.

The present chapter examines the extent to which quantification of dissolution from experiment is possible. Multivariate statistical techniques offer a powerful means of describing and analysing large datasets. Ordination can be used to describe the major patterns in the experimental data succinctly and effectively, both indirectly and directly (constrained by environmental data). The systematic relationships between measured dissolution parameters and changes in assemblage composition can be explored with numerical techniques (Pichon *et al.* 1992). Weighted averaging techniques (ter Braak 1987) are used to develop a predictive transfer function for empirically observed dissolution parameters for specific assemblages.

Additionally, the ranking of taxa in terms of experimental dissolution susceptibility can be applied to a separate salinity transfer function developed from diatom assemblages from the Northern Great Plains (Fritz 1990, Fritz *et al.* 1991). The transfer function can be adjusted by downweighting the influence of taxa and samples in the training set, according to relative resistance to dissolution, analogous to the approach of tolerance weighting, and similar to the transport index developed for estuarine diatoms by Juggins (1992). This is explored more fully in Chapter 7.

6.2 Aims of statistical analyses

Multivariate statistical procedures were applied to data from dissolution experiments as an

efficient means of describing and analysing a large and noisy dataset. Multidimensional datasets can be reduced to few independent axes which still retain the main underlying structure within the data using indirect and direct ordination. Indirect ordination (*e.g.* detrended correspondence analysis (DCA)) arranges the response (species) data without reference to measured environmental factors as an exploratory tool, and extracts latent variables. Direct ordination explores the relationship between measured environmental variables and species response. Techniques are available for examining linear (*e.g.* redundancy analysis (RDA)) and unimodal species response (*e.g.* canonical correspondence analysis (CCA)). Constraining the ordination by dissolution parameters can be used to derive a empirically-based predictive model. Both RDA and CCA are used in this context on experimental assemblages and groups of assemblages to produce dissolution transfer functions.

A final section applies the ecological concepts of optima and tolerance (derived from weighted averaging methods) to experimental dissolution parameters. This provides an alternative means of ranking species to that in Chapter 5, and compares the behaviour of taxa in "dissolution space" analysed with and without dissolution stages.

All ordination analyses were carried out using the FORTRAN program CANOCO (ter Braak 1987, 1990), version 3.12, which can perform both indirect and direct gradient analysis under unimodal and linear models of species response. Downweighting of rare species was routinely applied to all correspondence analyses, which can otherwise be unduly sensitive to rare taxa (Hill 1979 in ter Braak 1988). Ordination results from CANOCO were displayed graphically within CALIBRATE v.0.4 (Juggins 1994), which was also used for deriving weighted averaging transfer functions from species and environmental data.

6.3 Datasets

6.3.1 Species data

In order to compare diatom analyses with and without subdivision into dissolution stages, two families of matrices of species ("response") data were produced, identified hereafter by the prefix N (for "normal") and S ("stage-counted").

The first datasets (N1 and S1) formed the basis for all others, and were constructed as follows. Species data were transformed into percentages from raw counts, and any taxa which did not appear in at least one sample over 2% were excluded. This dataset (N1) formed the basis for the stage-counted version (S1), splitting each species included in this dataset into separate "taxa" according to the number of dissolution stages identified for each species. There was no

restriction on the percentages that taxa in this second dataset attained, except that any taxon with zero values for all samples were removed for convenience. The initial species datasets consisted of 88 samples and 78 (N1) and 213 (S1) taxa respectively, reflecting the modal number of dissolution stages identified for species. Both S and N species datasets were matched to the same appropriate matrix of environmental variables, depending on samples included.

Species data were not otherwise transformed during ordination except during redundancy analysis (RDA) in which case the percentage data were converted to ln(10x+1) form and standardised according to taxon error variance (option 4 within CANOCO for species centring/standardisation). This represents an intermediate position between standardisation to zero mean and unit variance (whereby all taxa are equally important in the ordination regardless of abundance in the data) and no transformation, whereby the ordination is dominated by taxa with the greatest variance, usually the most abundant taxa, even after log-transformation (ter Braak 1990).

6.3.2 Environmental data

Three variables associated with each sample were incorporated into an "environmental" dataset, together constituting the "dissolution process", and to which the assemblages were thought to respond. These were "experimental time" (relative to last sample time), "assemblage population change" (percentage remaining of original) and "dissolved silica" (ratio of dissolved to total initial solid silica). Raw data (expressed in the form of $(1-x)$ where negatively skewed) were transformed to an approximate unimodal distribution by taking logarithms (time, as log(T+1)) or the square root (population and silica), but were not explicitly standardised. The high degree of correlation between these transformed variables suggests they represent a common dissolution gradient (table 6.1). Sample diatom dissolution index (based on Flower's DDI, with a square root transformation) is included for comparison. Diatom dissolution index was only included in one analysis to describe the data (see below) as it is largely an artefact of the stage counting method.

A second set of dummy variables (a matrix of 1's and 0's) was also added to these four variables in analyses to factor out the effect of assemblage membership on samples. One assemblage acts as a reference, while samples belonging to the same assemblage are given a value of 1, and all other samples 0, in turn for all remaining assemblages.

The foremost problem in analysing the results of dissolution experiments on several different assemblages using programs developed for ecological applications is the validity of the

Table 6.1a - Correlations between untransformed environmental variables

Experimental Time	1			
Population Decline (%)	-0.84	1		
Dissolved Silica	0.85	-0.83	1	
Dissolution Index	-0.82	0.87	-0.83	1
	Experimental Time	**Population Decline (%)**	**Dissolved Silica**	**Dissolution Index**

Table 6.1b - Correlations between transformed environmental variables

Experimental Time	1			
Population Decline (%)	0.93	1		
Dissolved Silica	0.88	0.84	1	
Dissolution Index	0.79	0.79	0.81	1
	Experimental Time	**Population Decline (%)**	**Dissolved Silica**	**Dissolution Index**

ecological analogy inherent in the underlying models of species turnover. The four dissolution parameters are in a sense only "quasi-environmental variables" as species are not simply responding in the classical sense to true environmental parameters, which act unidirectionally affecting species distributions, but to an extent determine the "environment" as represented by measured dissolution variables. Population and silica loss can be viewed as cause and effect of species change, while time reflects dissolution progress, although to a degree less than DDI, which is excluded as an explanatory variable as it derives directly from the method of stage counting. Initial species composition is not related to the initial environment, but varies with each assemblage, while during the course of each experiment the same range of environmental gradients are experienced by distinct assemblages without the possibility of species exchange between flasks. The interpretation of analysis results should be viewed with these constraints in mind.

6.4 Statistical procedures

Collinearity is likely to be a problem within the explanatory variables, the uncritical inclusion of which tends to generate over-optimistic models (Okland & Eilertsen 1994). For this reason, forward selection of variables was routinely applied to explanatory direct analyses, although as pointed out by ter Braak (1990) this may overestimate the significance of variables, as in the case of multiple regression on a single variable. A diagnostic of collinearity is also provided by the Variance Inflation Factor (VIF) which is a measure of the multiple correlation R_j between an environmental variable j, and all other variables (ter Braak 1988):

$$VIF = \frac{1}{(1-R_j^2)} \qquad (1)$$

A variable with a large VIF implies high collinearity with other parameters and consequently little explanatory power in regression analysis. ter Braak suggests that the regression coefficient of a variable with a VIF over 20 is unstable and "does not merit interpretation" (ter Braak 1988). No variables with VIFs over 20 were included in direct ordinations.

Tests of significance are based on 99 permutations under a Monte Carlo simulation executed within CANOCO, and represents an exact level of probability (Verdonschot & ter Braak 1994). In all cases, forward selection of dissolution variables was made at p=0.05 or better.

6.5 Ordination of experimental data

6.5.1 Exploratory ordination

A detrended correspondence analysis (DCA) of the two species datasets pointed to the dissimilarity of the assemblages (first axis gradient length in standardised units of 11.69 for N1, 12.40 for S1) particularly assemblage I which formed an outlier to all other samples. Axis gradient length is a measure of the species distribution in the dataset, expressed as units of standard deviation (ter Braak 1987, ter Braak & Prentice 1988). Samples whose position along an axis differs by over about 4 s.d. units will share few species (ter Braak, 1987).

The isolation of assemblage I was only to be expected, given the counting problems of these samples, as there was almost no overlap between taxa after screening in this assemblage and any of the others (the one link was *Surirella ovalis*, which was only found significantly in assemblage B). As environmental data were incomplete for these samples, and they formed such a distinct outlier on the first two ordination axes assemblage I was removed from the species datasets, forming two new matrices N2 and S2. This reduced the number of samples to 80, and the number of taxa to 74 and 203, respectively.

A second DCA of N2 and S2, with the environmental variables plotted passively (ter Braak 1988), confirmed the large influence of assemblage I in the gradient length of the first axes, reduced to 7.37 s.d. and 8.10 s.d. respectively. This still represents very discordant assemblages, as the analyses verified the overriding dissimilarity of the assemblages rather than the similarity of the dissolution process as the major gradient within the datasets, with each assemblage forming a more or less discrete cluster in ordinational space in the first two axes.

No further samples were identified as outliers in data screening with respect to environmental variables. CANOCO flags samples with extreme environmental values as influential in terms of sample leverage for individual environmental variables (ter Braak 1990). A threshold of five times for univariate outliers. As the univariate leverage, **k**, is related to units of standard deviation (σ) by the relationship: $\sigma = (2\mathbf{k}\text{-}1)^{0.5}$, this equals 3 standard deviations from the mean for that variable (ter Braak 1990).

As a test of the hypothesis that there was a distinct dissolution gradient in the data, a series of canonical correspondence analyses (CCA) was carried out on N2 and S2. In CCA, the axes are restricted to be a linear combination of environmental variables ("restricted correspondence analysis", ter Braak 1987), and combines elements of both ordination and regression.

The role of assemblage type was compared against dissolution processes by carrying out three analyses for each dataset. In the first, all 3 dissolution and all 9 dummy variables (coded A/K

in the table) were chosen as environmental variables. In the second, only the dissolution variables were chosen, with no covariables. Lastly the effects of assemblage type were partialled out of the analysis by specifying the dummy variables of assemblage membership as covariables with the dissolution parameters constraining the ordination. The results of these ordinations are shown in table 6.2.

Although the assemblages differ to such a marked degree, there is still variation in the species data that is statistically significantly explained by dissolution processes, which can be extracted. It is possible to partition the total variance within each dataset into its constituent parts, in this case four components (Okland & Eilertsen 1994). Apart from an unexplained element, variance is uniquely associated with the dummy variables, the dissolution variables and an interaction between the two (table 6.3).

Assemblage type dominates the variance in both datasets, but cannot be partialled out adequately without losing a substantial amount of the variation linked to dissolution processes in both cases, although this effect is worse with N2 than S2 data. About the same amount of species variation is linked to dissolution processes in each case (about 10-11%), but of this only 14.9% (1.7/11.4) compared to 39.3% (4.2/10.7) can be assigned to these factors alone for N2 and S2 respectively. Dissolution factors account for a larger share of the explained variance with S2 (0.163) compared to N2 (0.133), although a greater proportion of species variance is unexplained using stage counting.

The trends in the data can be summarised on CCA biplots of sites, species and environmental variables with species scores as the weighted average of site scores (figures 6.1 & 6.2). CCA was applied to both N2 and S2, with assemblage type as covariables and silica, population and dissolution index included in the environmental variables by forward selection at p=0.01 (VIFs around 6 for DDI and population, and around 11 for silica in both cases).

Projection of the species points on the axes for each variable provides an estimate of the weighted average (optimum) of taxa along each gradient. The origin is centred with respect to these variables at their mean, and increase from this value in the direction of the vector, enlarged three times for clarity. The positions of projections of species points on the environmental variable axes relative to the origin implies an optimum higher or lower than the mean value within the dataset. Species are plotted at points corresponding to the centroid of their associated site scores, and biplot scores of environmental variables are (partial) covariances with the axes (ter Braak 1990).

Taxa tend to project along the three dissolution axes in both biplots (figure 6.1a & 6.2a) which

Table 6.2 - Canonical Correspondence Analysis Results

Species Data	Variables[1]	Covariables	$\Sigma\lambda_{can}$	Total Inertia	Variance explained (%)	Significance (Monte Carlo)
N2	S, T, P + A/K	None	4.594	5.382	85.4	0.01
S2	S, T, P + A/K	None	4.920	7.460	66.0	0.01
N2	S, T, P	None	0.612	5.382	11.4	0.01
S2	S, T, P	None	0.801	7.460	10.7	0.01
N2	S, T, P	A/K	0.093	5.382	1.7	0.01
S2	S, T, P	A/K	0.313	7.460	4.2	0.01

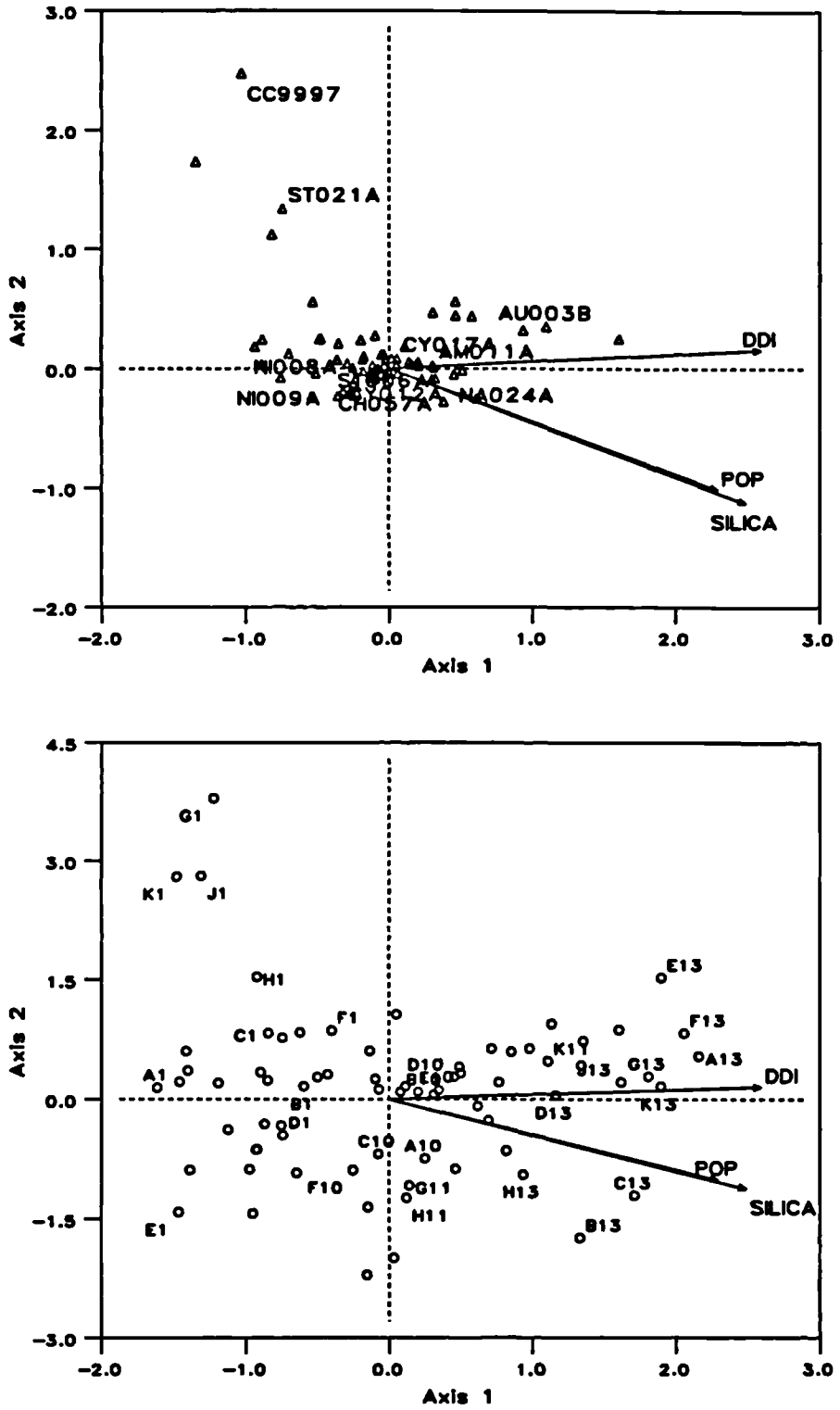
Table 6.3 - Variance partitioning (%) of N2 and S2 (CCA)

Data set	No. of taxa	Gradient length (DCA)	Assemblage type	Dissolution group	Interaction	Unexplained
N2	74	7.523	74.0	1.7	9.7	14.6
S2	203	8.094	55.3	4.2	6.5	34.0

[1] Variables are coded:

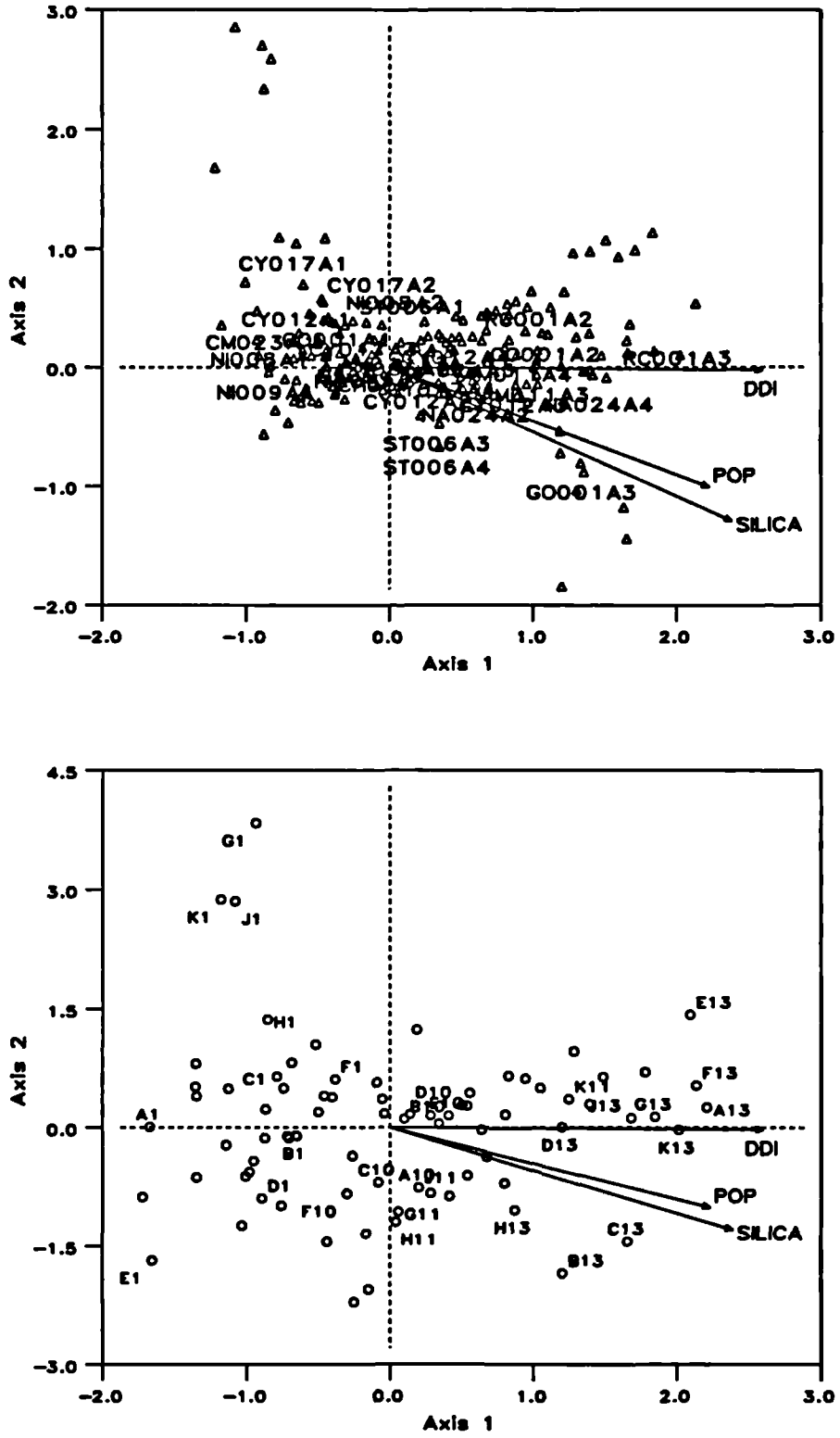
S - dissolved silica
T - experimental time
P - population decline

Figure 6.1a & b - CCA of N2 data



CCA of samples (bottom figure) and species (top figure) and environmental variables, with selected samples and species labelled. See text for explanation.

Figure 6.2a & b - CCA of S2 data



CCA of samples (b, bottom figure) and species (a , top figure) and environmental variables, with selected samples and species labelled. See text for explanation.

can be interpreted as a reflection of their dissolution susceptibilities, and similarly sites are arranged from well preserved to badly dissolved across the diagrams from left to right (figures 6.1b & 6.2b). On the S2 species biplot (figure 6.2a), stage subdivisions for a given species are separated along dissolution gradients, the centroid of which correspond to the species positions on the N2 species biplot (figure 6.1a). The last digit of the species code in figure 6.2a corresponds to the dissolution stage, from 1 (well preserved) to 4 (badly dissolved). As dissolution progresses, species stages act as taxa with dissolution optima increasing with stage number. Increasing dissolution is thus characterised by increasing relative abundance of higher stage taxa in each assemblage, although the relationship between silica dissolution and population loss depends on the species composition of each initial assemblage. These trends are illustrated for certain samples and taxa in the diagrams.

6.5.2 Ordination by flask

To test the hypothesis that dissolution was determining species change in the data, direct gradient analysis was performed on each flask (table 6.4). Separate datasets for each flask were produced from the N2 and S2 datasets, and matched with environmental data. An initial DCA for every assemblage suggested that none of the gradients were large enough to justify using unimodal models, as, under values of around 3 s.d. units, linear models are usually more appropriate (Verdonschot & ter Braak 1994, ter Braak 1987). Redundancy analyses (RDAs) were therefore carried out, with forward selection of three dissolution variables constraining the ordinations. These were then tested for statistical significance using the Monte Carlo permutation test (unrestricted, 99 permutations) on the trace or first canonical axis as appropriate. As with the canonical method of unimodal ordination (CCA), RDA involves both regression and ordination.

As might be anticipated, gradient lengths (GLs) are larger with stage counting as more species are identified within each assemblage. For example, samples in assemblage H show little change (GL=0.408, 5 taxa) counting without stages, but exhibit much more variation counting with stage (GL=1.130, 14 taxa). Explained variance is generally high for both data types, and is significant (p=0.01) for all assemblages using stage counts. Dissolved silica is the only parameter that approaches significance for two assemblages (D and K) counting without stages, which if allowed to constrain the ordination explains less than 40% of the species variance in both cases. In contrast, dissolution parameters significantly explain species response when these assemblages are counted with stages. Counting with stage subdivisions can increase the information extracted from dissolved samples, particularly where few species are present exhibiting a range of stages.

Table 6.4 - Redundancy analysis (RDA) results of separate assemblages

Data set	Number of taxa	Gradient Length (DCA)	Variables included[2]	Variance explained (%)	Significance (Monte Carlo)
Normal					
A	17	1.261	S	57.8	0.01
B	16	1.016	S	72.0	0.01
C	26	1.443	S, T	69.6	0.01
D	22	1.537	S[3]	38.3	0.06
E	22	1.283	S	54.7	0.01
F	17	0.659	S	55.2	0.01
G	13	1.206	T	41.8	0.02
H	5	0.408	S	47.6	0.02
J	12	0.894	T	51.7	0.01
K	11	1.306	S[3]	37.9	0.07
Stage counted					
A	46	2.937	S	50.4	0.01
B	44	1.666	S, T	75.7	0.01
C	67	1.977	S, T	65.9	0.01
D	61	2.327	S	48.3	0.01
E	59	2.692	S	54.3	0.01
F	44	1.458	S, T	69.4	0.01
G	38	2.262	T	52.1	0.01
H	14	1.130	S	44.3	0.01
J	34	2.119	T	56.0	0.01
K	32	3.104	P, T	68.3	0.01

[2] Variables are coded:

S - dissolved silica
T - experimental time
P - population decline

[3] No variables were significant at a level of p=0.05. Silica is included here as p(S)=0.06

6.5.3 Ordination of groups of flasks

As a test of the role of dissolution as sample heterogeneity increased, eight assemblages were combined into four groups of two, based in part on the divisions suggested by a TWINSPAN (v. 2.1a; Hill 1979) two-way table with default options (table 6.5). These groupings agreed with the clusters observed with DCA ordinations on the entire datasets, combining assemblages A & B (group 1), D & E (group 2), C & F (group 3) and J & K (group 4). Further ordination was carried out on these groups.

Table 6.6 lists the results of these experiments. Separate DCAs preceded direct analysis by linear or unimodal response model, depending on the gradient length measured by DCA. Again, linear models employ redundancy analysis while the technique of canonical correspondence analysis (CCA) best serves unimodal responses over a wider range (ter Braak & Prentice 1988).

As expected, average gradient lengths for the amalgamated assemblages are larger than those of the flasks considered individually for both counting methods, but the difference between GIs for stage counted samples relative to normal methods is less than in the individual assemblages. Where gradient length was around 3 s.d. units, both CCA and RDA were applied to the data, but there was little difference in the variance of species data explained (in CCA given by the ratio of all canonical eigenvalues to the total inertia). There was no difference in the statistical significance (unrestricted, n=99) under either model in these cases.

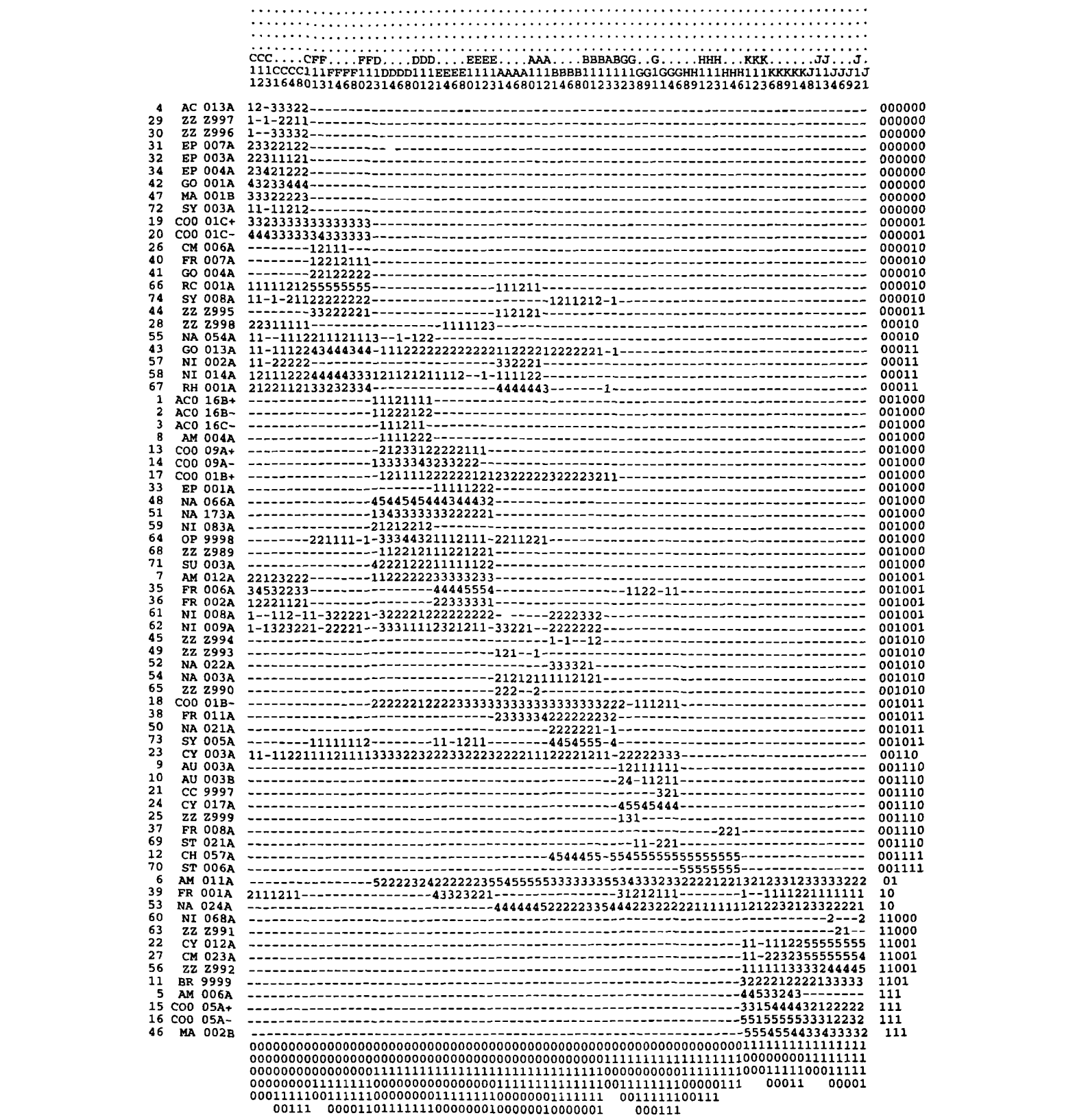
Slightly more variance is explained under normal counting for groups 1 and 2, and about the same for group 3, all significant at p=0.05 or better. Measured dissolution variables had no statistically significant explanatory power for group 4 with normal counting, but explained over 40% for the stage counted version (p=0.03). Increasing sample heterogeneity from individual flasks (table 6.4) to N2 and S2 datasets (tables 6.2 & 6.3) is associated with decreasing (but still significant) explanation by the environmental variables (dissolution). Such relationships can form the basis for developing transfer functions to estimate dissolution parameters.

6.6 Weighted averaging methods: dissolution transfer functions

6.6.1 Introduction

The weighted averaging (WA) approach implicit in correspondence analysis can be used to derive transfer functions relating environmental variables to species abundance, by a two stage

Table 6.5 - TWINSPAN two-way table of N2 species data



Coding: 1=0-2%, 2=2-5%, 3=5-10%, 4=10-20%, 5=20+%

Table 6.6 - Direct gradient analysis (RDA and CCA) of combined assemblages

Group/flasks (count strategy)		Number of taxa	Gradient length[4]	Variables included[5]	Variance explained (%)	Significance (Monte Carlo)
Normal						
1	A, B	24	3.027	S, T	55.5	0.01
2	D, E	28	1.697	S, T	60.7	0.01
3	C, F	32	2.667	S	19.3	0.05
4	J, K	13	2.281	none[6]	---	---
Stage counted						
1	A, B	62	3.624	S, T	53.3	0.01
2	D, E	79	2.936	S, T	54.3	0.01
3	C, F	84	2.841	S	19.5	0.01
4	J, K	36	3.828	S, T	43.7	0.03

[4] Results are from RDAs for gradient lengths less than 3 s.d. units, and for CCAs over this (see text).

[5] Variables are coded:

S - dissolved silica
T - experimental time
P - population decline

[6] No variables were significant with forward selection at p=0.05

process of regression and calibration. Weighted averaging has been applied in an ecological context since the 1940s although it is only relatively recently that critical appraisal of the underlying statistical theory has established the technique on a sounder theoretical basis (ter Braak 1987). The weighted averaging method is an intuitively straightforward and robust alternative to the computationally demanding techniques of classical maximum likelihood (ML), and Gaussian logit regression and calibration, under certain conditions of unimodal species response (ter Braak & Looman 1986, Juggins 1992).

For WA to approximate the ML estimated species optimum:

1 Site scores are equally spaced over the range of species occurrence over the environmental variable, and closely spaced relative to species' tolerance

and for environmental calibration under WA to approach that of ML:

2 Species optima are equally distributed along the environmental gradient over a large interval around each site

3 Equal species maxima and tolerance (or at least independent of optima).

Techniques employing WA tend to be stable even where these conditions are not strictly met. For example, CCA is robust despite relaxation of these assumptions as long as species response remains unimodal (ter Braak 1987).

Recent studies have shown that weighted averaging, and its tolerance-weighted version, may perform as well or better than ML methods, particularly in reconstructing palaeoenvironments from fossil assemblages under "no-analogue" circumstances (Birks *et al.* 1990, Juggins 1992) under which circumstances it interpolates rather than extrapolates values (Hutson 1977). Weighted averaging disregards species absences, while ML considers both presences and absences equally (Birks *et al.* 1990, ter Braak & Looman 1986). Weighted averaging may therefore be better suited to ecological data which include many zero values, reflecting the general asymmetry in value between presence and absence in ecology (ter Braak 1987).

The following summary is based on that given in Juggins (1992) using the standard symbol conventions:

y_{ik} - the proportion of a taxon k (of m) at site i (hereafter y_i)
x_i - the observed value of the environmental variable at site i (of n)

The species optimum (u_{wa}) is simply estimated from the average of the values of an environmental variable in which the species is found, weighted by the species abundance :

$$\hat{u}_{wa}=\sum_{i=1}^{n} y_i x_i / \sum_{i=1}^{n} y_i \qquad (2)$$

The range or tolerance (t_{wa}) of a species is defined as the standard deviation between the species optimum and the observed value of the variable across all sites, weighted by the abundance:

$$\hat{t}_{wa}=\sqrt{\sum_{i=1}^{n} y_i (x_i-\hat{u})^2 / \sum_{i=1}^{n} y_i} \qquad (3)$$

Calibration of environmental variables under WA is then a weighted average of the optima of the species present:

$$\hat{x}_{wa}=\sum_{k=1}^{m} y_k \hat{u}_k / \sum_{k=1}^{m} y_k \qquad (4)$$

Tolerance usually varies between species, violating condition 3 above, but this can be standardised by downweighting the influence of species on calibration at a site (equation (4)) by a factor related to their tolerance:

$$\hat{x}_{wa}=\frac{\sum_{k=1}^{m} y_k \hat{u}_k / \hat{t}_k^2}{\sum_{k=1}^{m} y_k / \hat{t}_k^2} \qquad (5)$$

During the process of WA regression and WA calibration, the environmental gradient is shrunk

as averages are calculated twice. A "deshrinking" procedure of linear regression of the actual against the inferred ***x*** values is used to expand the range, which can take the form of inverse or classical regression (Birks *et al.* 1990, Juggins 1992). Inverse regression minimises the errors on the whole model (in the form of producing the smallest root mean squared error, RMSE) while classical regression expands the range at the edge of the gradient by taking values further from the mean (greater deshrinking). Either can be used depending on the particular application for the model.

Weighted averaging has been successfully applied to diatom data implicitly or explicitly for environmental reconstruction, for example of pH (Gasse & Tekaia 1983, Allott *et al.* 1992, Birks *et al.* 1990) and salinity (Fritz 1990, Juggins 1992, Cumming & Smol 1993), and compares favourably to classical techniques based on a linear least squares model, and unimodal models involving ML.

6.6.2 Dissolution transfer functions

Weighted averaging techniques were applied to the combined assemblages of groups 1-4 for both N and S data. WA methods are best applied where gradient length is about 3 s.d. or above, and produces increasingly unreliable estimates as species behave more monotonically (ter Braak & Prentice 1988). These authors suggest that over the range ("window") of 1.5-3 s.d., linear and non-linear methods can both be usefully applied to data. In the cases where gradient lengths fall into this category (groups 2N, 3N, 4N, 2S & 3S), a comparison with linear methods was made using calibration within CANOCO of each environmental variable in turn as the only constraining variable under RDA. In this case, the species-environment correlation with the first (sole) canonical axis provides an estimate of **r** (ter Braak 1988).

Table 6.7 summarises the results of the analyses. The variables involved were chosen on the basis of their inclusion in the direct ordination analyses carried out previously (table 6.6). For each variable for each dataset, figures for the RMSE and coefficient of determination (r^2) are given for each of four weighted average calibrations, standard and tolerance weighted average, and for each, a jackknife estimate of the reliability of the transfer function. The RMSE is calculated as from the observed and inferred values of ***x***:

Table 6.7 - Dissolution transfer functions: Groups 1-4

Data set	Method	RDA r^2		Silica		Time	
		Silica	Time	RMSE	r^2	RMSE	r^2
Group 1N (A, B)	WA	---	---	1.658	0.594	0.338	0.638
	WA_{tol}			1.492	0.671	0.334	0.646
	Jack WA			2.080	0.380	0.542	0.107
	Jack WA_{tol}			2.154	0.368	0.531	0.134
Group 2N (D, E)	WA	0.785 p=0.01	0.605 p=0.05	0.950	0.703	0.369	0.569
	WA_{tol}			0.906	0.730	0.350	0.613
	Jack WA			1.160	0.559	0.469	0.310
	Jack WA_{tol}			1.181	0.544	0.461	0.327
Group 3N (C, F)	WA	0.810 p=0.07	---	1.191	0.687	---	---
	WA_{tol}			1.332	0.608	---	---
	Jack WA			2.061	0.152	---	---
	Jack WA_{tol}			2.010	0.202	---	---
Group 4N (J, K)	WA	0.554 p=0.29	---	1.645	0.697	---	---
	WA_{tol}			1.582	0.720	---	---
	Jack WA			2.882	0.077	---	---
	Jack WA_{tol}			2.855	0.087	---	---
Group 1S (A, B)	WA	---	---	0.977	0.859	0.311	0.693
	WA_{tol}			0.951	0.866	0.218	0.850
	Jack WA			1.346	0.735	0.427	0.436
	Jack WA_{tol}			1.744	0.601	0.326	0.667
Group 2S (D, E)	WA	0.951 p=0.01	0.859 p=0.01	0.457	0.931	0.248	0.805
	WA_{tol}			0.369	0.955	0.198	0.876
	Jack WA			0.603	0.886	0.336	0.642
	Jack WA_{tol}			0.576	0.910	0.325	0.729
Group 3S (C, F)	WA	0.906 p=0.02	---	0.730	0.882	---	---
	WA_{tol}			0.774	0.868	---	---
	Jack WA			1.512	0.552	---	---
	Jack WA_{tol}			1.441	0.614	---	---
Group 4S (J, K)	WA	---	---	1.630	0.702	0.329	0.716
	WA_{tol}			1.247	0.826	0.285	0.786
	Jack WA			2.089	0.512	0.432	0.511
	Jack WA_{tol}			1.723	0.681	0.383	0.617

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \hat{x}_i)^2}{n}} \quad (6)$$

The jackknife technique is a method of computer-intensive validation, in which each sample in turn is excluded from the reconstruction. A number of reconstructions equal to the number of samples is generated, from which jackknife estimates of species' optima, tolerances, coefficient of determination, and error of prediction for an environmental variable can be derived, under both WA and tolerance methods (Birks 1993). In CALIBRATE, the jackknife can be conditioned onto groups of samples, which permits resampling within data blocks. Jackknifing was conditioned onto as many groups as there were assemblages in each dataset analysed.

The datasets that perform best are those stage-counted whether WA or linear calibration methods are used, with tolerance downweighting often an improvement over simple WA. Linear methods may appear to fit the data as well or better than unimodal models in many situations, especially where gradient lengths are shorter, but high correlations may not be statistically significant. Jackknife validation for WA demonstrates that initial estimates of RMSE and r^2 may not reflect the actual error involved. High r^2 values for WA and WA_{tol} are always overestimates of the goodness of fit to the data, especially for type N data which usually display a dramatic fall after jackknifing (compare the results of groups 1N & 3N for example) in contrast to type S data.

Dissolved silica (Jack WA_{tol} r^2=0.910) and experimental time (Jack WA_{tol} r^2=0.729) can both be accurately estimated within group 2S, and although dissolved silica explains only 19.5% of the species variation in group 3S (table 6.6) the jackknifing r^2 estimates of silica within this dataset are still reasonably good (Jack WA r^2=0.552, Jack WA_{tol} r^2=0.612), particularly when compared to its type N counterpart. The analysis suggests that once the relationship between dissolution and assemblage composition has been established, dissolution variables can be reconstructed from stage-counted samples more reliably and consistently than with standard counting methods.

6.6.3 Species ranking by dissolution optima

The use of "optima" and "tolerance" in the context of dissolution parameters is by analogy only, as these are not responses in an ecological sense. Rather, they are used to explore the

dissolution behaviour of species in what is a theoretical dissolution space. The order of species optima along dissolution gradients can be interpreted as an approximate dissolution ranking. Figure 6.3 shows the optima and range (optima +/- tolerance) for silica for the 74 taxa included in N2, from figures listed in table 6.8. Figure 6.4 compares the ranking based on WA optima of dataset N2 and ***A***-ranks (Chapter 5) for taxa common to the two systems (49 species). Although dissolved silica as a dissolution parameter is not exactly comparable between different assemblages many species considered without reference to dissolution state show a WA optimum that corresponds to inferred robustness, in general agreement with the rank ordering developed in Chapter 5.

There is a slight tendency for WA ranks to underestimate resistance to dissolution of taxa considered robust by ***A***-ranking, and *vice versa* for dissolution susceptible taxa (high ***A***-ranks). Some inconsistencies may result from samples with low diversity. For example, assemblage H (without stage subdivision) includes samples that are on the limit of application of WA methods with less than 5 species (ter Braak & Prentice 1988). Pichon *et al.* (1992) removed samples depauperate in species before Q-mode analysis of dissolution experiments.

Species split into stages behave analogously (figure 6.5 & table 6.8), almost all dissolution taxon with an associated optimum and tolerance increasing with the sequence in dissolution stages, and together bracketing the species' optimum.

"Tolerance" in this case can be related to the residence time of a valve within a dissolution category, large tolerances reflecting the resistance of a given stage as identified under LM. Early stages tend to have the longest residence times, which reflects the method of identification. For many species a relatively large amount of dissolution can occur before a pristine valve appears dissolved enough to unambiguously allocate to stage two, although the longevity of later stages depends more on specific valve structure, with some end stages (such as *Amphora libyca*, *Cyclotella meneghiniana*, *Cy. caspia*, *Surirella ovalis*, *Stephanodiscus niagarae*, *Gomphonema olivaceum* and *Synedra pulchella*) structurally robust, compared to their intervening stages.

6.6.4 Species behaviour in dissolution space

Unimodal distributions of species along environmental gradients are implicit in WA methods. The suitability of ecological analogy to characterise the response of species, and dissolution taxa, to the dissolution environment can be demonstrated graphically by examining the distribution of species in dissolution space. The terminology of species "response" is again used as a convenient analogy to explain dissolution behaviour, and not with any implied ecological

Table 6.8 - Species/stage silica WA optima (u) & tolerance (t)

WA rank	Code	Taxon	Species Optimum	Tolerance	Dissolution stages 1 u	1 t	2 u	2 t	3 u	3 t	4 u	4 t
1	ZZZ999	Cymbella H17	9.44	1.84			6.00	1.96	9.81	1.96	9.49	1.66
2	AU003B	Aulacoseira granulata v angustissimma	8.27	3.65	1.60	3.59	9.23	1.32	9.16	1.36		
3	MA002B	Mastogloia elliptica var dansei	7.08	2.89	5.30	2.98	7.21	2.29	8.59	1.88	8.91	1.74
4	NA024A	Navicula oblonga	6.81	2.79	4.55	2.39	7.25	2.27	7.85	2.56	8.11	2.26
5	CY012A	Cyclotella caspia	6.77	3.05	4.96	2.89	7.49	2.36	8.52	2.55	7.40	3.42
6	AU003A	Aulacoseira granulata	6.74	3.71	4.18	3.33	9.12	1.35	9.81	1.96		
7	CM023A	Cymbella pusilla	6.47	3.05	5.46	3.00	7.49	2.77	8.06	2.42		
8	AM006A	Amphora coffaeaformis (all)	6.39	3.69	2.91	3.07	7.92	2.73				
9	CY017A	Cyclotella quillensis	6.31	2.93	3.70	3.16	4.63	3.22	5.93	2.45	7.26	2.58
10	ZZZ998	Cymbella sp	6.14	2.34	4.51	2.68	6.47	2.21	7.50	1.13	6.95	1.57
11	AM011A	Amphora libyca	6.04	2.58	4.43	2.23	6.45	1.82	7.52	2.11	8.08	2.33
12	BR9999	Brachysira aponina	5.88	3.22	4.73	3.26	6.84	2.90				
13	CO005A-	Cocconeis pediculus -	5.72	3.00	4.91	3.04	7.01	2.49				
14	EP001A	Epithemia sorex	5.65	1.64	4.71	2.05	6.63	0.89	5.71	0.74		
15	ZZZ991	Nitzschia sp	5.65	2.09	5.12	1.96	5.95	2.09				
16	FR011A	Fragilaria lapponica	5.58	2.85	4.55	2.41	7.71	2.46	8.94	1.50		
17	EP004A	Epithemia turgida	5.54	2.96	4.73	2.67	6.05	3.02	8.36	1.67	8.66	1.96
18	CH057A	Chaetoceros cysts	5.44	2.51	5.44	2.51						
19	FR006A	Fragilaria brevistriata	5.28	2.20	4.83	2.24	6.48	1.37	7.47	1.40		
20	RH001A	Rhopalodia gibba	5.27	2.13	4.66	1.90	6.38	2.00	6.55	2.21		
21	EP003A	Epithemia argus	5.16	2.84	4.38	2.67	6.87	2.05	8.66	1.96	8.66	1.96
22	GO004A	Gomphonema C	5.11	2.02	4.69	1.83	6.94	1.89				
23	ST006A	Stephanodiscus niagarae	5.02	2.22	4.13	2.10	5.30	2.00	6.40	1.73	6.60	2.07
24	CO005A+	Cocconeis pediculus +	5.00	3.11	4.57	3.03	6.37	3.11				
25	FR001A	Fragilaria pinnata	4.89	2.49	4.12	2.21	7.13	1.32	9.25	1.12		
26	ZZZ995	Gomphonema pumilum group	4.87	1.98	4.64	1.93	6.12	1.77	7.62	1.96		
27	ZZZ992	Nitzschia E35	4.87	3.36	4.46	3.28	6.96	2.90				
28	EP007A	Epithemia adnata	4.80	2.76	4.36	2.70	5.96	2.40	7.61	2.90		
29	MA001B	Mastogloia smithii var lacustris	4.79	2.65	3.62	2.16	5.26	2.51	7.07	2.21	7.44	2.38
30	CM006A	Cymbella cistula	4.77	2.63	4.55	2.56			8.01	1.96		
31	SU003A	Surirella ovalis	4.77	1.86	3.85	1.81	5.45	1.27	6.06	1.38	6.11	1.96
32	RC001A	Rhoicosphenia curvata	4.71	1.87	4.39	1.64	6.37	2.14	8.15	0.46		
33	FR007A	Fragilaria vaucheriae	4.71	2.25	4.31	2.01	6.46	2.71	8.01	1.96		
34	CO001C-	Cocconeis placentula var lineata -	4.66	2.25	4.42	2.11	5.33	2.52				
35	CO001B-	Cocconeis placentula var euglypta -	4.66	2.26	4.30	2.13	5.74	2.30				
36	FR002A	Fragilaria construens	4.60	2.09	4.34	2.11	6.01	1.20	6.49	1.96		
37	NA054A	Navicula veneta	4.56	1.49	4.14	1.45	4.94	1.38	5.63	1.21		
38	NI014A	Nitzschia amphibia	4.48	1.88	4.06	1.72	5.88	1.75				

Table 6.8 - Species/stage silica WA optima (u) & tolerance (t)

WA rank	Code	Taxon	Species Optimum	Species Tolerance	Dissolution stages 1 u	1 t	2 u	2 t	3 u	3 t	4 u	4 t
39	SY008A	Synedra pulchella	4.40	1.97	3.62	1.51	6.21	1.65	8.01	1.96		
40	CY003A	Cyclotella meneghiniana	4.35	2.28	2.75	1.35	4.44	1.75	5.48	1.72	5.75	2.36
41	GO013A	Gomphonema parvulum	4.35	1.80	3.88	1.54	5.47	1.80	6.04	1.87		
42	CO001C+	Cocconeis placentula var lineata +	4.28	2.06	4.15	2.02	5.06	2.20				
43	CO001B+	Cocconeis placentula var euglypta +	4.20	2.07	3.78	1.90	5.65	1.87				
44	ZZZ993	Navicula cf perminuta S13 (A)	4.15	2.30	3.86	2.50	4.95	2.00				
45	AM012A	Amphora pediculus	4.12	1.92	3.59	1.68	5.00	1.70	6.56	1.19	6.90	1.14
46	NA003A	Navicula radiosa	4.12	2.19	2.65	1.09	3.48	1.83	3.90	2.32	4.84	2.17
47	ZZZ994	Gomphonema sp	4.09	2.18	3.71	2.10	5.02	2.42				
48	ZZZ989	*Stephanodiscus cf minutulus*	3.97	1.63	3.41	1.32	4.44	1.63	2.96	1.41		
49	OP9998	Opephora olsenii	3.96	1.93	3.33	1.74	4.87	1.88	5.04	1.44		
50	ZZZ990	Pennate girdle	3.96	2.37	3.96	2.37						
51	NA066A	Navicula capitata var capitata	3.88	1.67	3.21	1.48	4.49	1.50	5.36	1.48		
52	SY005A	Synedra fasciculata	3.77	1.89	3.33	1.62	4.99	1.87	5.16	2.72		
53	NI083A	Nitzschia constricta	3.72	1.62	3.00	1.72	4.11	1.20				
54	ZZZ997	Denticula sp	3.70	2.63	3.02	1.78	8.66	1.96				
55	CO009A+	Cocconeis neothumensis? +	3.65	1.32	3.65	1.31	3.81	1.88				
56	GO001A	Gomphonema olivaceum	3.61	2.07	3.14	1.67	5.91	1.91	7.44	3.70		
57	AM004A	Amphora veneta	3.58	1.37	2.50	1.14	4.63	0.38	4.00	0.82	4.86	0.46
58	CO009A-	Cocconeis neothumensis? -	3.55	1.40	3.47	1.39	4.18	1.42				
59	AC016B+	Achnanthes delicatula v delicatula +	3.52	1.68	2.52	1.13	4.46	1.53				
60	NA173A	Navicula erifuga	3.52	1.59	2.90	1.15	3.75	1.73	4.03	1.60		
61	NI008A	Nitzschia frustulum	3.51	1.56	3.11	1.28	4.96	1.68				
62	AC016B-	Achnanthes delicatula v delicatula -	3.49	1.49	2.64	1.20	4.29	1.28				
63	ST021A	Stephanodiscus minutulus	3.35	3.50	1.72	3.92	4.70	2.88				
64	NI002A	Nitzschia aff fonticola var 1	3.28	1.93	3.17	1.79	5.63	3.07				
65	NA021A	Navicula cincta cf f minuta	3.20	1.64	2.78	0.97	3.14	1.13	8.31	1.96		
66	SY003A	Synedra acus	3.19	1.82	3.00	1.62	5.14	3.73				
67	NI009A	Nitzschia palea	2.86	1.34	2.66	1.13	4.26	1.73				
68	AC013A	Achnanthes minutissima (all)	2.77	1.84	2.61	1.72	5.01	2.21				
69	AC016C-	Achnanthes delicatula v hauckiana -	2.65	1.09	2.28	0.82	3.65	1.02				
70	NA022A	Navicula halophila	2.51	0.73	2.32	0.63	2.66	0.75	3.12	0.77		
71	ZZZ996	Diatoma moniliformis	2.43	1.35	2.21	1.26	3.83	1.03				
72	FR008A	Fragilaria crotonensis	2.15	1.15	2.07	1.08	4.01	1.96				
73	NI068A	Nitzschia bergii	2.14	1.63	2.29	1.63	1.13	1.96				
74	CC9997	Cyclostephanos tholioformis	1.64	3.67	1.30	3.92	5.12	1.96				

Figure 6.3 - WA optima & tolerance for silica (N2 data)

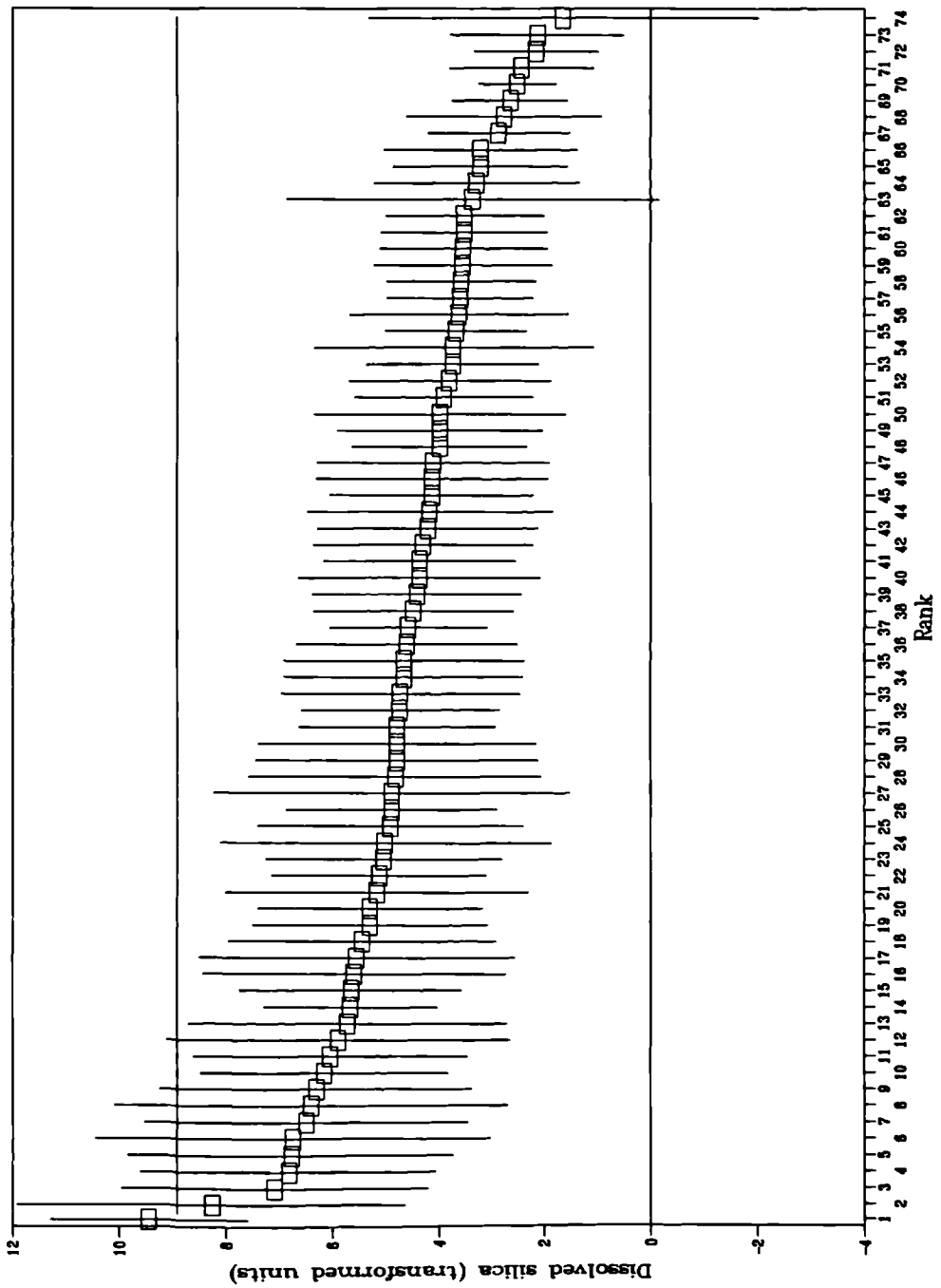


Figure 6.4 - Relative WA optima (silica) & A ranking

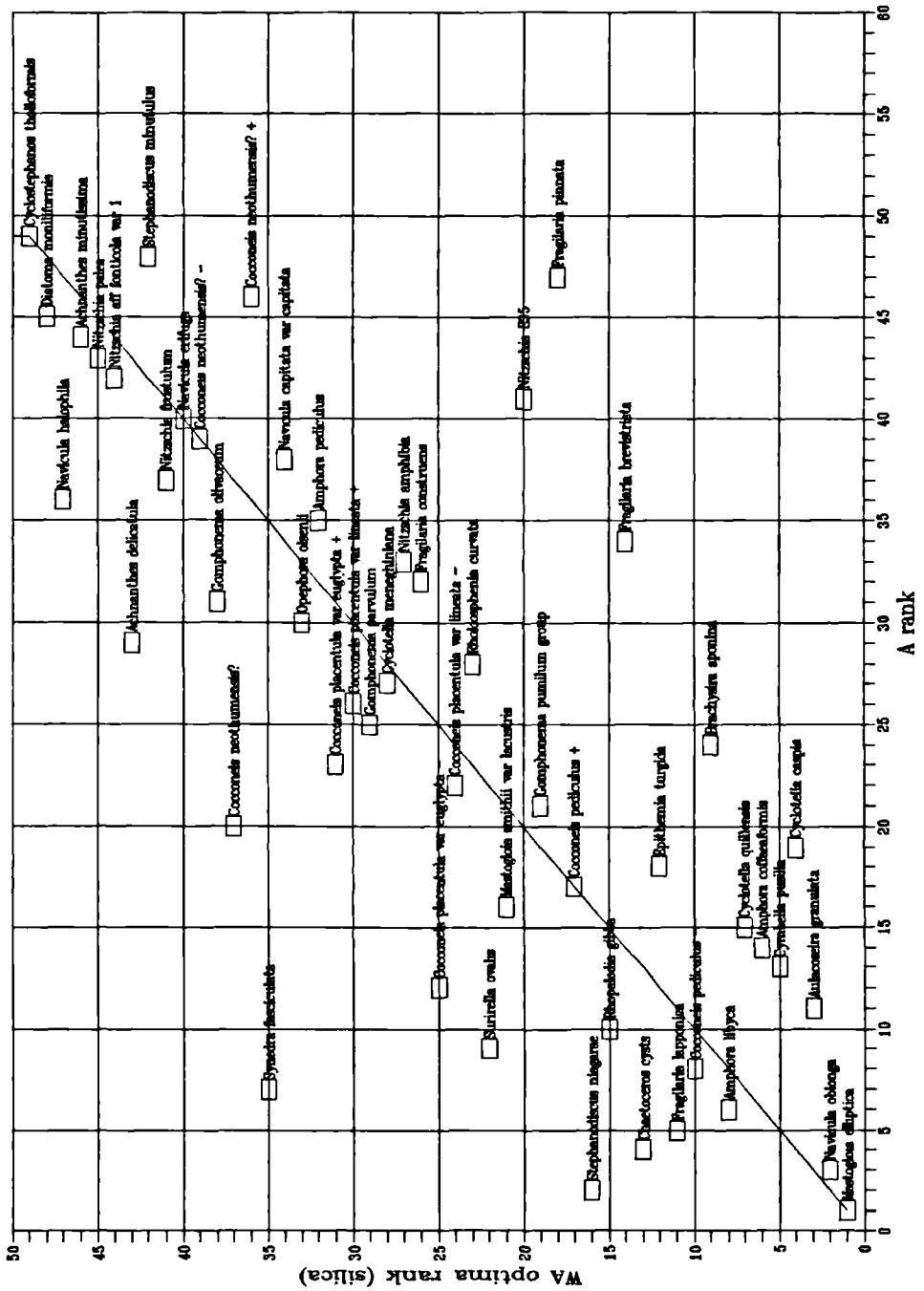
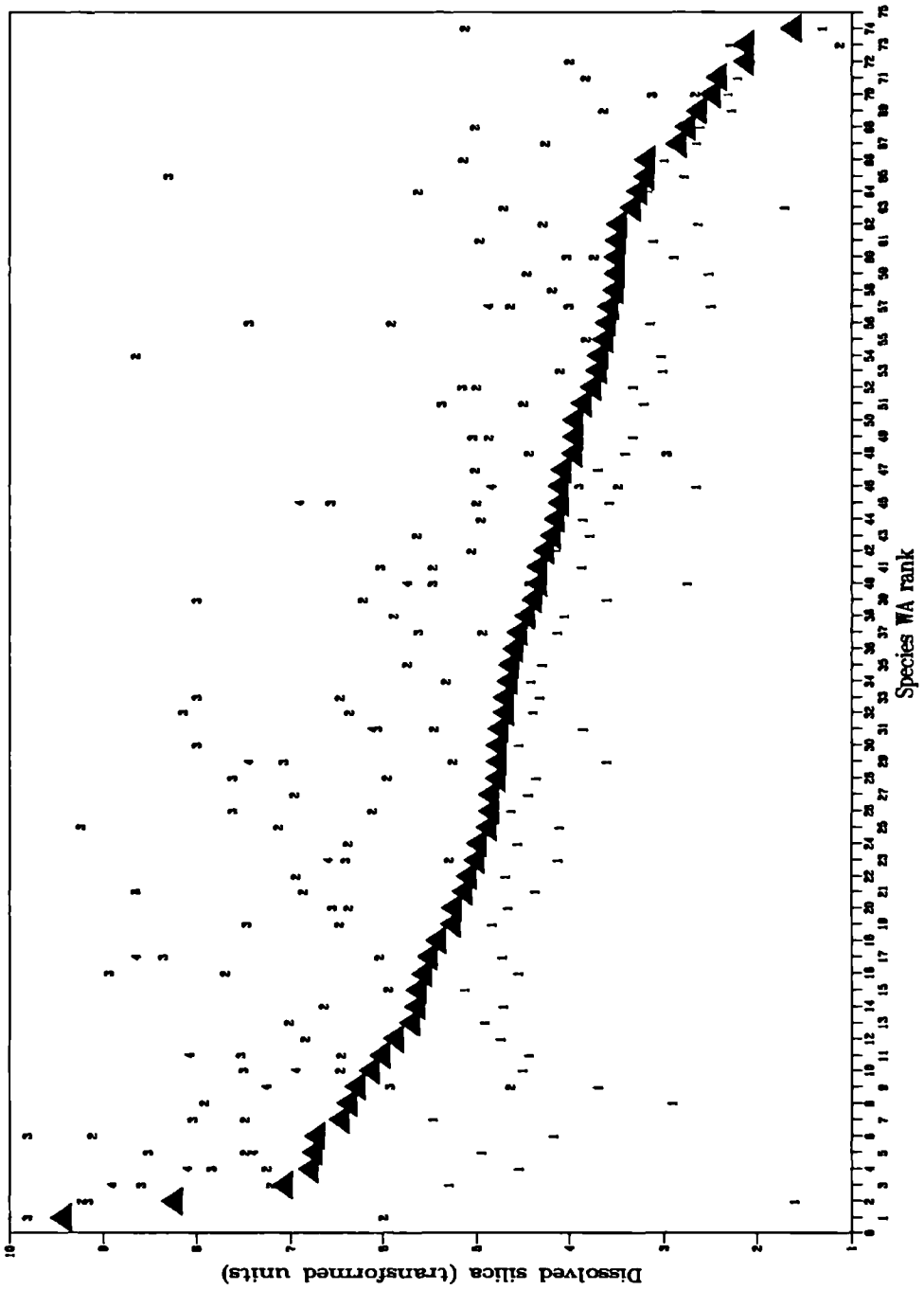


Figure 6.5 - WA optima (silica) for species and stages



meaning.

Species responses can be modelled by ML logistic regression, which fits the distribution to a Gaussian curve in the form:

$$\log_e \left(\frac{y}{1-y}\right) = a - \frac{(x-u)^2}{2t^2} \qquad (7)$$

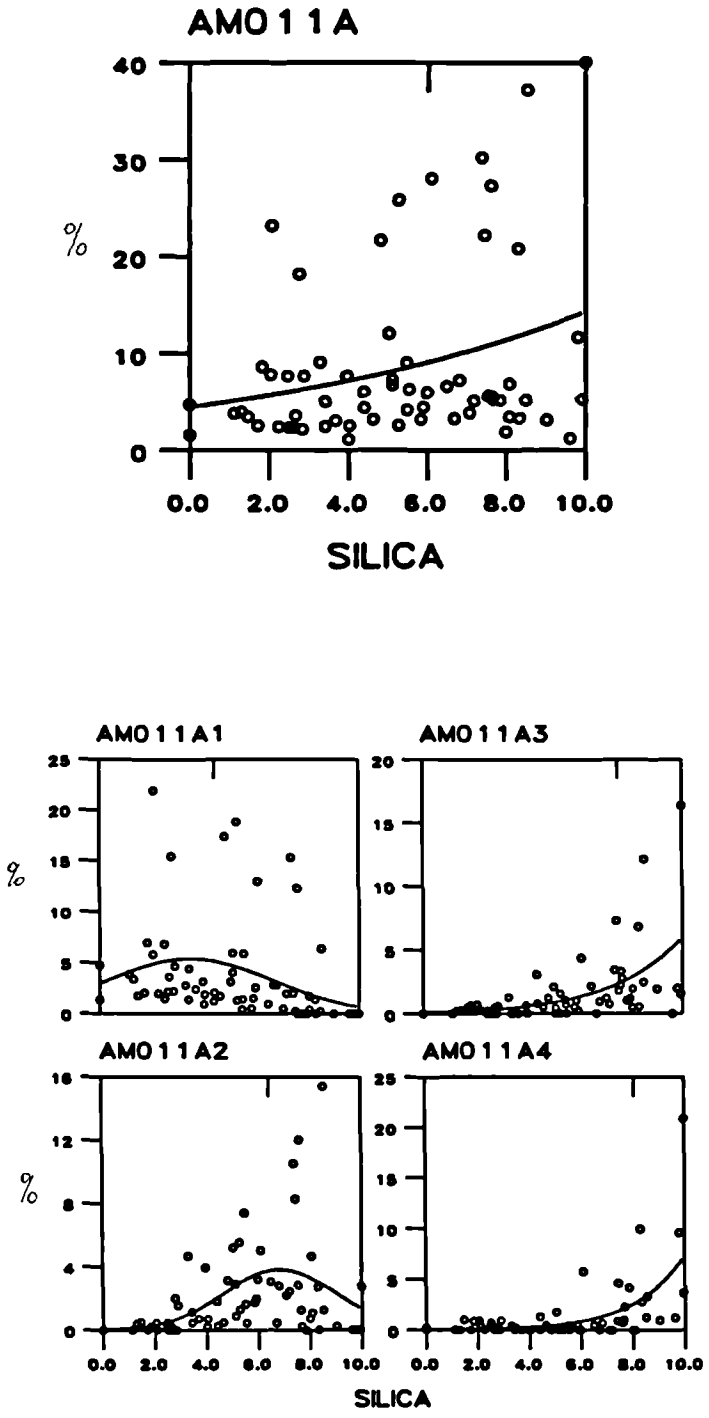
where y is again the proportion of a taxon (probability of occurrence) and ML logistic regression estimates tolerance, optimum and maximum relative abundance (Juggins 1992, ter Braak 1987). Some examples of species' response to dissolved silica (transformed units) fitted by Gaussian logit regression are shown for both species and stage divisions (figures 6.6-6.11). Weighted averaging estimates of the taxon silica optimum are also shown. If a species occurred in any sample, all samples from that flask were included, to take into account meaningful zero abundance values. As weighted averaging ignores these values, in contrast to ML methods, not all samples can be indiscriminantly incorporated as some zero values reflect dissolution (a "real response"), while others merely the fact that every species was not initially present in every assemblage.

For several species, and dissolution taxa, the ML optimum falls outside the range of silica values, suggesting a linear response across the gradient. Species responses to such quasi-environmental variables demand caution in interpretation, but demonstrate the conditions under which WA can be used to estimate species optima under ML, where a sufficient gradient is sampled relative to the tolerance to permit expression of a unimodal response. Splitting species into dissolution taxa suggests that each does have its separate "niche" in the dissolution sequence, succeeding each other in order.

6.7 Discussion

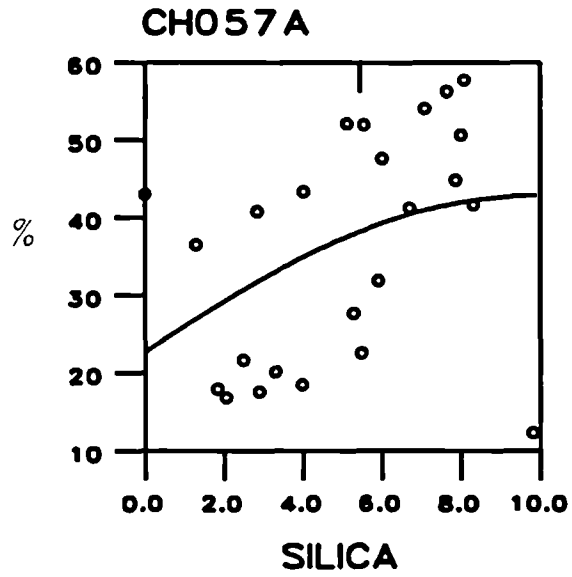
Assemblage composition was initially chosen to cover a range of species with limited overlap, which by necessity implies little correspondence between samples from different assemblages in which the environmental variables cannot uniquely determine the species "response". As assemblages are amalgamated, the degree of variance explained by dissolution processes falls, but remains statistically significant. Dissolution effects are consistent and significant enough to be detected across very different assemblages ("environments") by multivariate methods based on models of community ecology which cannot be expected to be fully applicable to such experiments.

Figure 6.6 - *Amphora libyca*



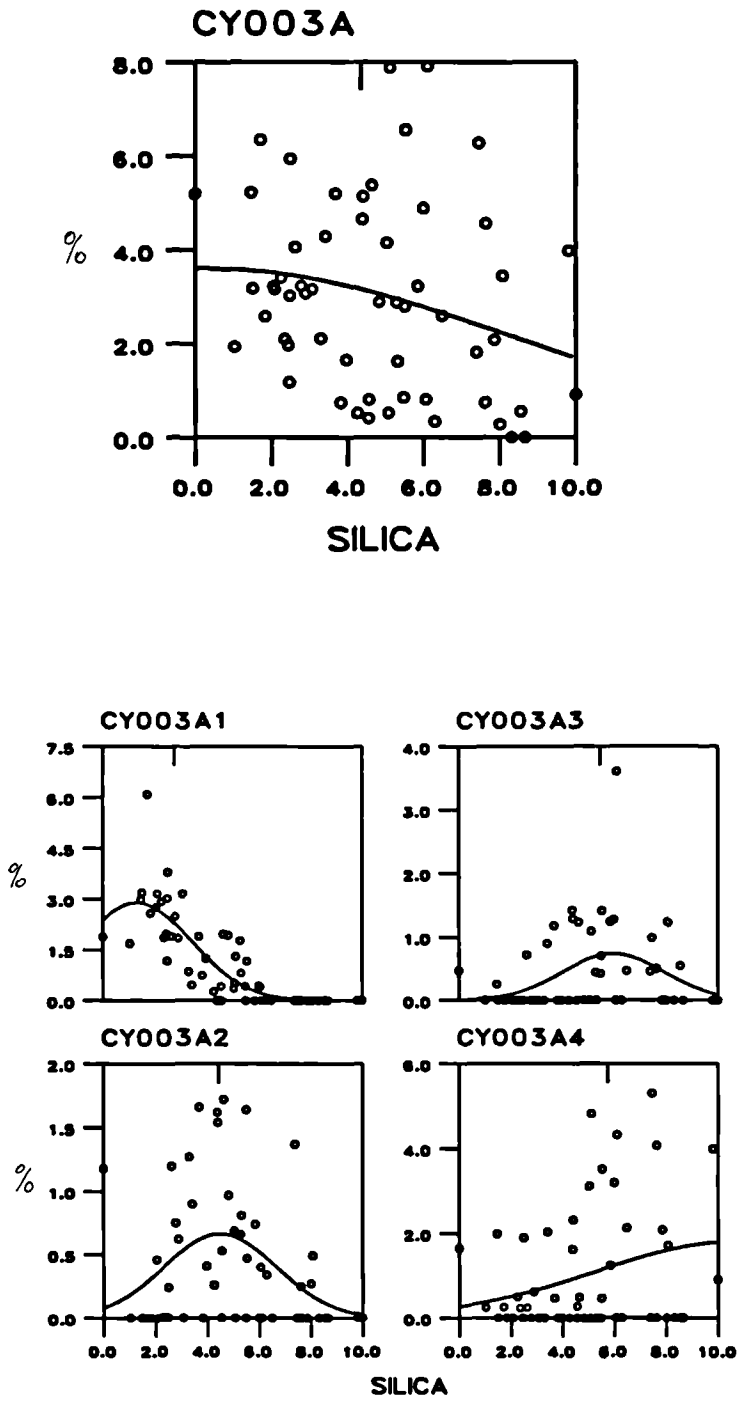
Occurrence of species (upper figure) and stages (lower figures, coded by stage category) with respect to dissolved silica (as square root of percentage). Also plotted are the optima for each taxon, as estimated by WA (tick mark at top of diagrams) and the modelled response under logistic regression (predicted unimodal fit).

Figure 6.7 - *Chaetoceros* cysts



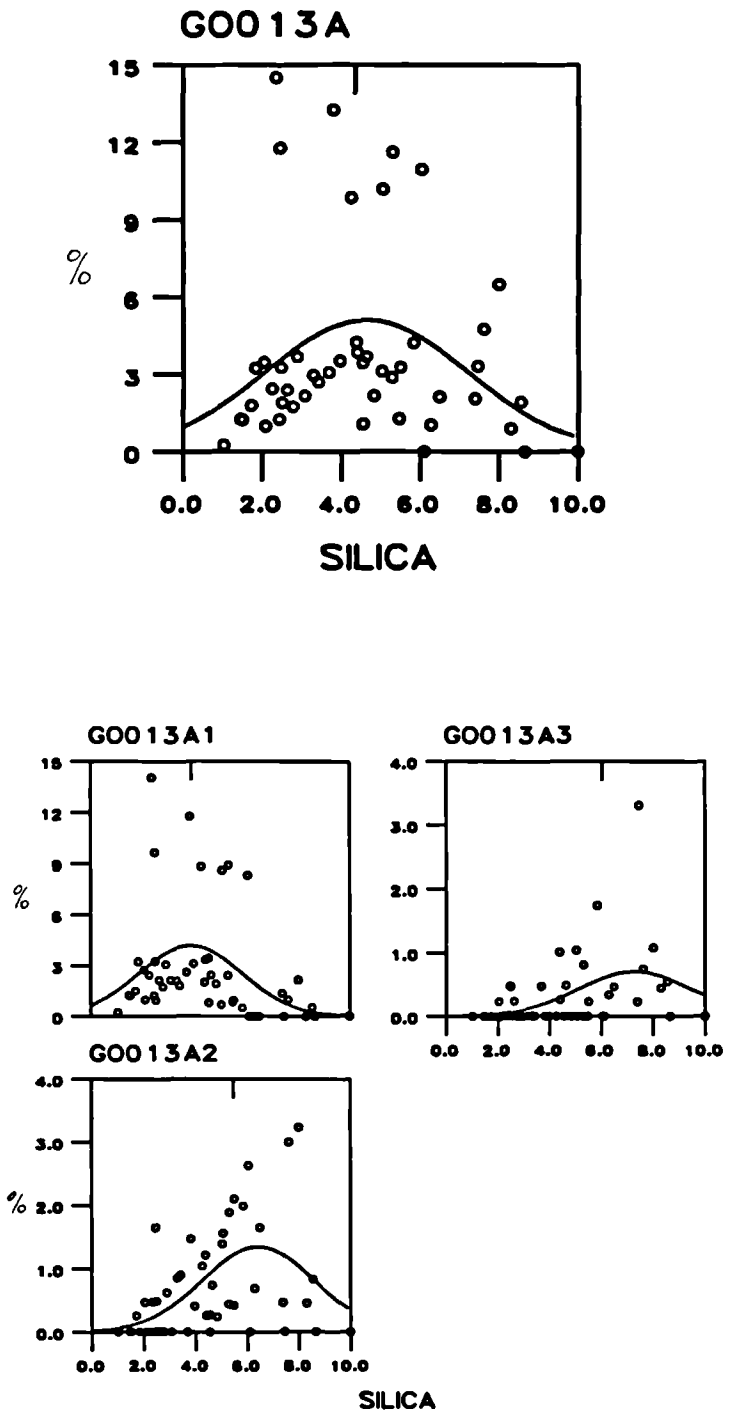
Occurrence of taxon with respect to dissolved silica (as square root of percentage). Also plotted are the optimum, as estimated by WA (tick mark at top of diagram) and the modelled response under logistic regression (predicted unimodal fit). No stage subdivisions were reliably identified for *Chaetoceros* cysts.

Figure 6.8 - *Cyclotella meneghiniana*



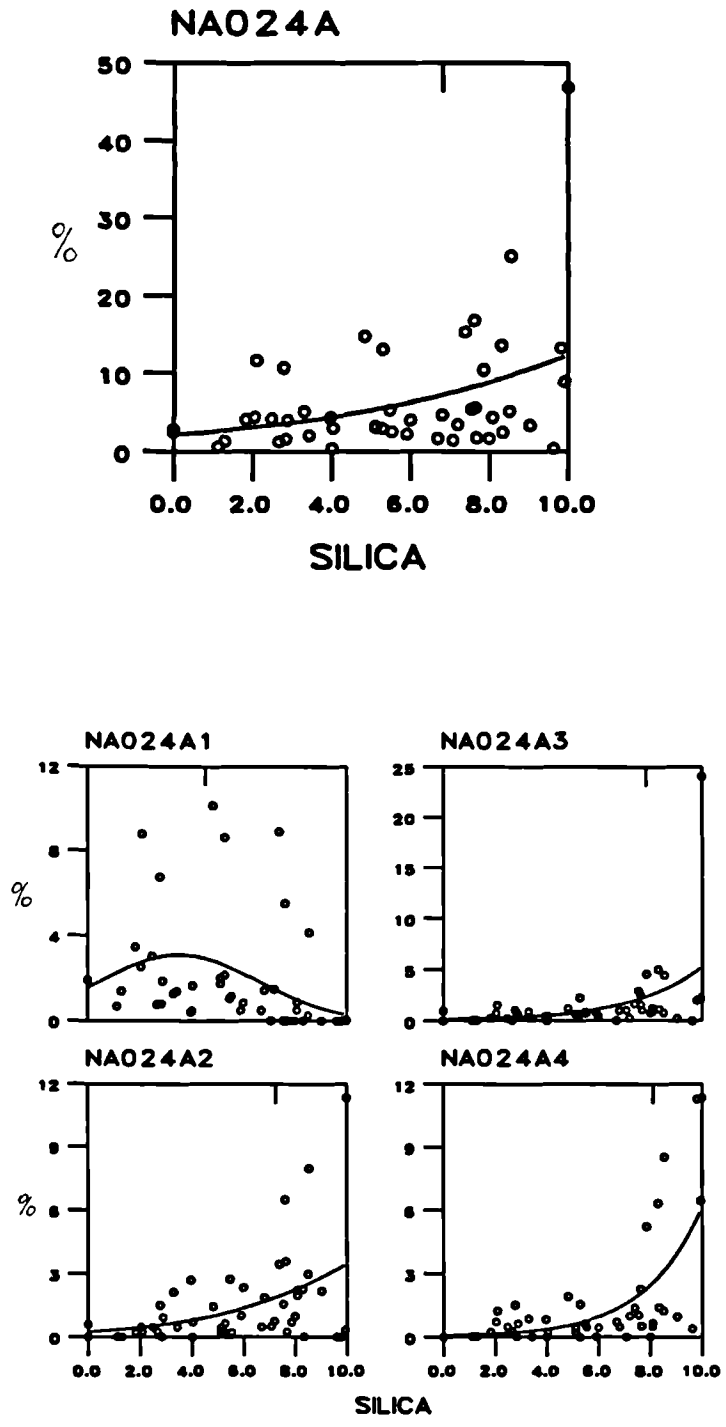
Occurrence of species (upper figure) and stages (lower figures, coded by stage category) with respect to dissolved silica (as square root of percentage). Also plotted are the optima for each taxon, as estimated by WA (tick mark at top of diagrams) and the modelled response under logistic regression (predicted unimodal fit).

Figure 6.9 - *Gomphonema parvulum*



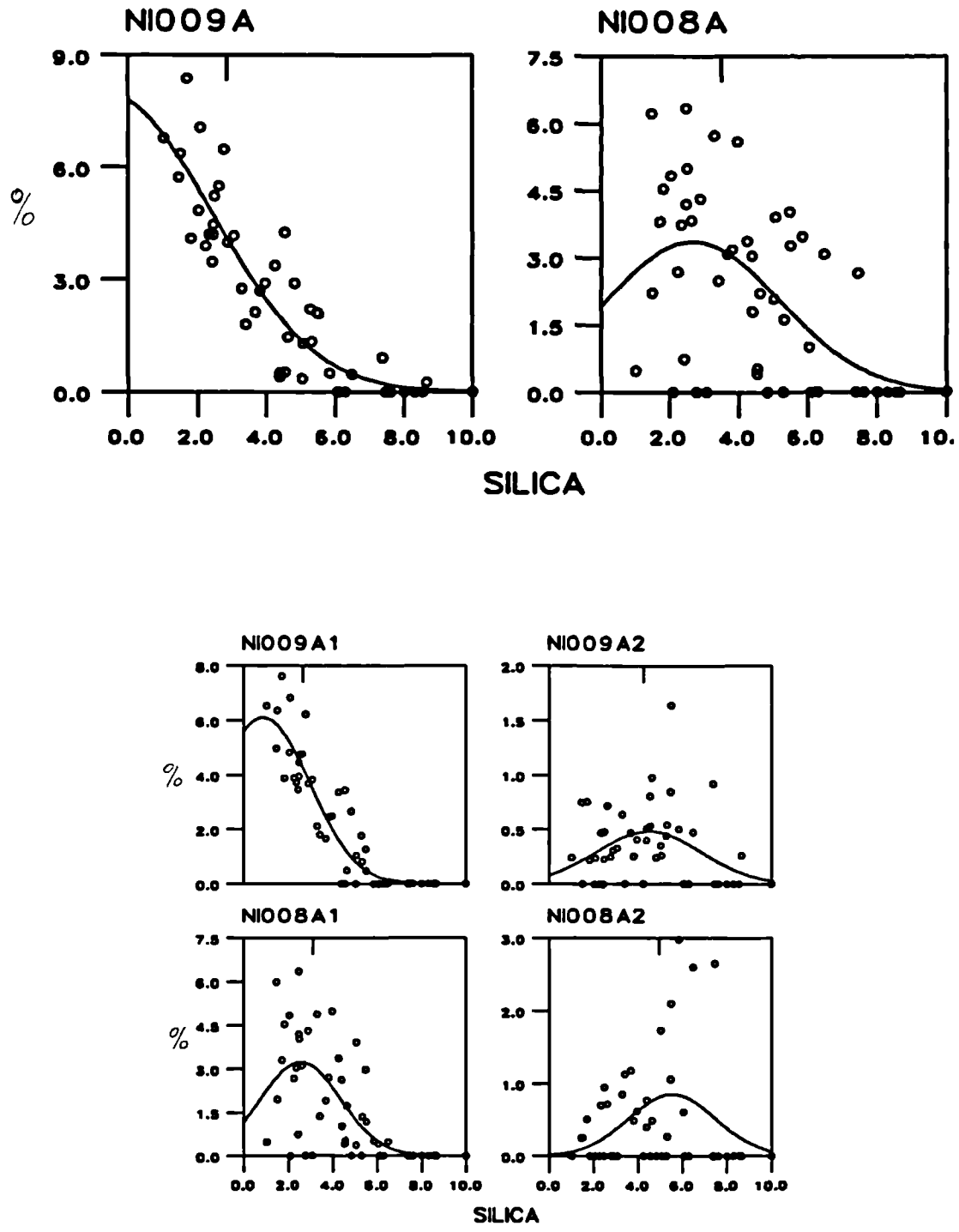
Occurrence of species (upper figure) and stages (lower figures, coded by stage category) with respect to dissolved silica (as square root of percentage). Also plotted are the optima for each taxon, as estimated by WA (tick mark at top of diagrams) and the modelled response under logistic regression (predicted unimodal fit).

Figure 6.10 - *Navicula oblonga*



Occurrence of species (upper figure) and stages (lower figures, coded by stage category) with respect to dissolved silica (as square root of percentage). Also plotted are the optima for each taxon, as estimated by WA (tick mark at top of diagrams) and the modelled response under logistic regression (predicted unimodal fit).

Figure 6.11 - *Nitzschia palea* (NI009A) & *Nitzschia frustulum* (NI008A)



Occurrence of species (upper figure) and stages (lower figures, coded by stage category) with respect to dissolved silica (as square root of percentage). Also plotted are the optima for each taxon, as estimated by WA (tick mark at top of diagrams) and the modelled response under logistic regression (predicted unimodal fit).

Each flask is a closed system, and each represents a separate "biogeographic realm" as far as interaction between assemblages is concerned. The same reasoning that enabled different assemblages to be comparable in a system of ranking creates inconsistencies when multivariate ordination is applied to the data. Ordination expects assemblages to change gradually (ter Braak 1994 in press), according to common environmental gradients that determine communities, while species that occur in several flasks will behave according to the assemblage context. Species distributions, and the parameters that describe them (optima and tolerance) are only strictly valid in the particular circumstances of each assemblage, as distinct from the relationship between population change and dissolution index for a specific taxon. Given an assemblage, the methods of weighted averaging or linear regression and calibration on experimentally dissolved samples, enhanced with stage counting, can be used to infer loss of silica or population of natural samples derived from the same assemblage quantitatively, and it is reasonable to expect with a high degree of confidence.

In one sense, the problem of microfossil preservation can be avoided by ignoring badly preserved samples (Imbrie & Kipp 1971), which although good advice, is unfeasible in many situations, where there may not be scope for choice. Perfect preservation must be considered the exception rather than the rule, and it is in this light that dissolution must be viewed. A dissolved sample may often be the best source of environmental data in many situations, and can still provide ample information.

Previous work involving multivariate analysis of biological data which has focused explicitly on aspects of preservation have applied linear models predominantly, particularly methods based on PCA (Thunell 1976, Thompson 1976, Hutson 1977, Hutson 1978, Peterson & Prell 1985). Thunell (1976) applied PCA to the downcore variation of four carbonate dissolution parameters on each of 5 marine sediment cores from the Gulf of Mexico and evaluated the usefulness of each indicator on the basis of the correlation with the first axis (assumed to be a "unified measure of dissolution") which accounted for an average of 56.9% of variation in the data (range 41.2%-75.4%). Test fragmentation and benthic foraminiferal proportion were found to be the best indices, in contrast to $CaCO_3$ content.

In a similar vein Peterson & Prell (1985) employed R-mode analysis on 6 dissolution indices for 43 surface sediment samples from the eastern equatorial Indian Ocean. A Composite Dissolution Index (the principal factor scores of the first axis) was extracted which explained 82.6% of the variance, which suggested that dissolution was the major determinant of differences in carbonate sediments in the region. Dissolution is highly non-linearly depth-dependant, and increases sharply at the lysocline.

Hutson (1977) compared the behaviour of five types of transfer function under no-analogue conditions (high dissolution samples) and found that all methods lost accuracy when calibrated against samples from one dissolution category (low dissolution surface samples) although weighted averaging provided the least erroneous estimates. The difference in kind as well as degree between undissolved (plankton), low and high dissolution samples was demonstrated by Hutson (1978). Transfer functions developed with Q-mode factor analysis (a form of PCA) from contemporary datasets from each category from the same oceanic regions could not be reliably applied to samples in different dissolution states, particularly in the case of high dissolution samples which could not be linearly related to low dissolution assemblages. A possible solution is to calibrate transfer functions on samples with a large range of dissolution conditions (Hutson 1978).

Recent studies on the quantitative estimation of biogenic silica loss in marine sediments have employed controlled dissolution of surface sediments to develop dissolution indices and transfer functions for particular assemblages (Pichon *et al.* 1992, Shemesh *et al.* 1989), which correspond to oceanic regions. Pichon *et al.* (1992) found that a Q-mode analysis on 166 surface samples, including 42 dissolution samples, extracted a fourth axis which explained 6.6% of the total species variance. Their procedure involved Q-mode factor analysis and a subsequent regression of environmental variables on principal components extracted (Imbrie & Kipp 1971). "Factor 4" was unrelated to ecological gradients but strongly related to measured silica loss in the experimental samples, via a quadratic function in factor 4 sample loadings, with r=0.90, S.E.E.=15%. Experimental samples consisted of aliquots of surface sediments from 5 box cores dissolved in 2M Na_2CO_3 at 60C, for periods from 5 minutes to 120 hours, with colourimetric determination of supernatant silica after centrifuging at 1500 rpm for 5 minutes (Pichon *et al.* 1992, following Shemesh *et al.* 1989). Counts were made of 300-450 individuals for less dissolved samples but under 100 specimens could be identified by the latter stages.

The surface sediments comprised three zonal assemblages and two endemic species (*Nitzschia kerguelensis* and *Thalassiosira lentiginosa*) in differing proportions, with 32 diatom taxa and 2 silicoflagellate genera identified. These initial surface sediments are similar relative to the datasets N2 and S2 in the present dissolution experiments, and indeed were chosen due to high communalities and low proportions of late-glacial taxa (Pichon *et al.* 1992). Dissolution parameters can be reliably estimated for similar situations in which initial assemblage composition remains relatively homogenous by calibration through empirical experiment, as dissolution behaviour at the assemblage level is dependant on initial composition.

Larger initial environmental gradients may be accommodated by considering several initial assemblages separately, and developing transfer functions for each one (perhaps by analogy

with Bartlein & Webb 1985) with the option of employing WA methods and stage counting to improve calibration. In all situations, the relationship between population (silica) loss for individual taxa with dissolution index may provide meaningful information on dissolution processes depending on the taxa involved.

Transfer functions can be developed from experimental dissolution data, but because dissolution parameters are only quasi-environmental, species responses cannot be generalised between very different initial assemblages. Several approaches to the problem can be suggested, which can successfully address the quantification of dissolution, with stage counting often representing an improvement over normal techniques. The application of stage counting and dissolution ranking to reconstruction of other environmental variables is discussed in Chapter 7 using the example of the NGP salinity transfer function. The implications of the approach are explored on a short core from Spiritwood Lake, North Dakota.

Chapter 7
Palaeolimnological application

7.1 Introduction

The Northern Great Plains (NGP) dataset has been successfully used to build a salinity transfer function based on WA techniques from surface sediment samples from lakes across a range of salinities in North and South Dakota, and Saskatchewan, Canada (Fritz 1990, Fritz *et al.* 1991, Fritz *et al.* 1993). Transfer functions based on this approach have performed unevenly when tested against a known salinity record from Devil's Lake, North Dakota, and have tended to underestimate the highest salinity excursions, although differentiating between high and low salinity episodes (over 10 g/l TDS) and providing good correspondence during fresher conditions. A potential source of error lies in the unequal preservation state of samples, particularly but not exclusively at higher salinities. The differential preservation of species affects the development of accurate estimates of species parameters (optima and tolerance), feeding into inaccuracies in estimated salinity on calibration.

This chapter examines the effect on the transfer function of weighting species and species according to species susceptibility to dissolution in two ways. Firstly, the effects of this approach are assessed on the NGP training set in terms of improvements to the model compared to the unweighted (control) dataset. Secondly, a core from Spiritwood Lake is used to test of the differences in performance of the transfer function when different systems of weighting are applied, and how this influences the salinity and environmental reconstruction at this site.

7.2 The Northern Great Plains dataset

Of the 64 lakes included in the original study, 9 contained no diatoms in the surface sediments, and the remaining 55 were subsequently included in a salinity transfer function, based on the correlation between measured salinity and the first canonical axis in a CCA (Fritz 1990). These data were used in all analyses in the present study, and comprise percentage counts for all taxa identified in any sample at 2% or above, and an associated value of salinity for each lake (as **S**-units, $\log_{10}$(salinity) in g/l TDS). After such screening, 172 taxa are included from counts of 400-600 valves from each sample, although this was reduced in cases of poor preservation (Fritz *et al.* 1991). Salinity varies between 0.7-270 g/l (Chapter 2), and although there are differences in ionic composition, and trophic status in the contemporary lake systems, salinity is a dominant gradient across the lakes affecting diatom distribution. The principal effect of pH, which is uniformly high (above 8) across the sites, on the diatom flora is not through ecological

response of the living communities (Fritz 1990, figure 5) but the differential dissolution of death assemblages.

7.3 The Northern Great Plains salinity transfer function

7.3.1 Calibration within CANOCO

This study assesses whether salinity predictions can be improved by introducing a system of variable weightings to the surface sediment data, that takes the preservation quality of the samples in the training set into account. This procedure generates several transfer functions, and these are applied to passive samples from a short core.

All calibration was performed within CANOCO, according to the procedure outlined by ter Braak (1988). If samples are constrained by a single environmental variable, whether under linear (RDA) or unimodal (CCA) models, the species-environment correlation affords an estimate of **r** between observed and estimated values for a parameter. A measure of the stability of the regression is given by the proportion of the first to the second (first unconstrained) axis (Kingston *et al.* 1992, ter Braak 1988). This ratio is a gauge of how important the fraction of species variance captured by the constraining variable is in the context of the entire species data. For comparison, weighted averaging was also applied to unweighted datasets within CALIBRATE, which permits the choice between inverse or classical regression, and allows jackknifing validation of the transfer functions generated.

An initial CCA within CANOCO on the full original dataset (NGP1) constrained by salinity provided a value for r^2 of 0.83 (p=0.01; table 7.1), with a RMSE of 0.245 **S**-units. Salinity by itself explains only 4.5% of the species data, but nevertheless can be efficiently recovered from the biological data across the entire environmental gradient. Surprisingly, one sample was flagged as a potential outlier in the dataset, according to the leverage tests routinely applied within CANOCO v3.12. The univariate leverage of Bitter Lake in the unweighted data is 6.3, corresponding to a value over three standard deviations from the mean. On closer examination there appeared several reasons for constructing a second dataset excluding the Bitter Lake sample, which has a highly unusual diatom composition as well as an extreme salinity of 270 g/l (2.43 **S**-units, compared to the next largest value of 1.62).

The species composition of the Bitter Lake sample essentially consists of one taxon, *Cyclotella quillensis* (CY0017A) in a relative abundance of 95% (N_2 = 1.11). This by itself is insufficient grounds for rejection, but the modelled distribution of this taxon is highly affected by this site. Figure 7.1a & b shows the change in WA and ML optimum (the latter modelled by logistic regression) for this species when Bitter Lake is included or not in the distribution. Excluding the sample lowers the WA optimum, but more significantly restores a more ecologically reasonable

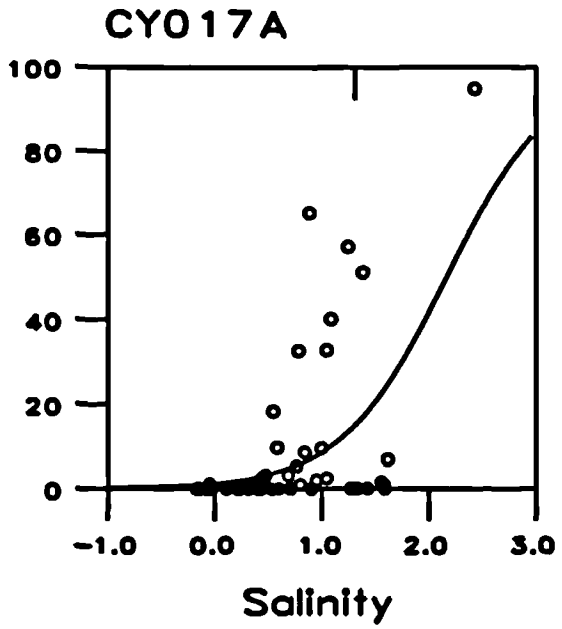
Table 7.1 - NGP1 & NGP2 WA calibration (CANOCO)

Data set	No. lakes	$\%\lambda_1$	λ_1/λ_2	r^2	Apparent RMSE	Significance (Monte Carlo)
NGP1	55	4.5	0.816	0.834	0.245	0.01
NGP2	54	4.7	0.910	0.857	0.206	0.01

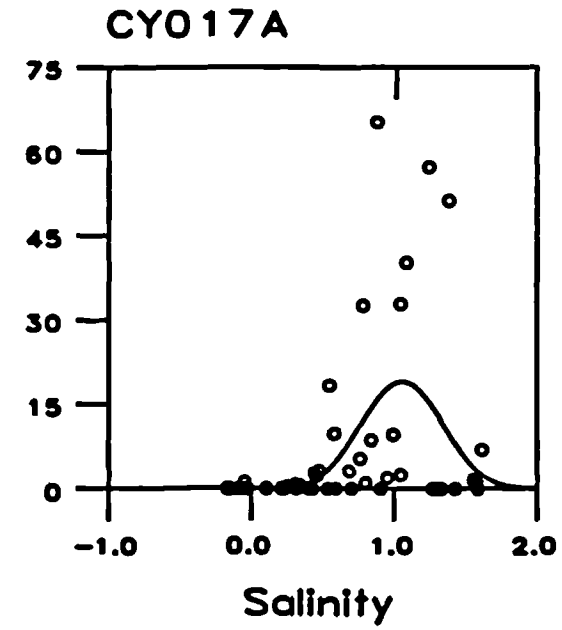
Table 7.2 - NGP1 & NGP2 WA calibration (CALIBRATE)

Data set	Deshrinking	Model	WA	WA_{tol}	WA_J	WA_{Jtol}
NGP1	Classical	r^2	0.835	0.845	0.666	0.678
		RMSE	0.245	0.236	0.332	0.334
	Inverse	r^2	0.835	0.845	0.663	0.678
		RMSE	0.224	0.217	0.321	0.315
NGP2	Classical	r^2	0.859	0.899	0.714	0.764
		RMSE	0.206	0.171	0.279	0.256
	Inverse	r^2	0.859	0.899	0.710	0.762
		RMSE	0.191	0.162	0.273	0.248

Figure 7.1 - *Cyclotella quillensis* (CY0017A)



a



b

Abundance of *Cyclotella quillensis* including (a, upper figure) and excluding (b, lower figure) Bitter Lake sample with respect to salinity (S-units). The estimated WA salinity optimum (tick mark at top of diagrams) and that derived from logistic regression (predicted unimodal fit) nearly coincide with Bitter Lake removed.

unimodal response with the optima in general agreement.

This prompted a re-examination of the original lake data, which includes two Bitter Lakes, one of which was excluded from analysis due to a very poor diatom preservation (Fritz 1990, Fritz *et al.* 1993). It seems that the environmental data for Bitter Lake, Saskatchewan, has been linked to the diatom count from Bitter Lake, Day County, South Dakota (salinity 23.53 g/l). Checking the original count sheet and slide (collected by Prof. R.W.Battarbee, 1982) confirms that this has happened, which figure 7.1 suggests would fit in with the known distribution of *Cyclotella quillensis*. Consequently a second NGP dataset (NGP2) was created ignoring this sample.

A second salinity-constrained CCA excluding this sample showed an immediate improvement in r^2 (0.86, p=0.01), RMSE (0.206 S-units) and species variance explained (table 7.1). Figures 7.2 & 7.3 display the estimated against the observed salinity for the dataset of 55 and 54 lakes respectively. Bitter Lake appears as an under-estimated outlier on the figure 7.2, which accounts in some part for the fall in RMSE between the two different datasets.

Inspection of the residuals between the two datasets (figures 7.4 & 7.5) also points to improvements in the transfer function, as there is less structure to the residuals with Bitter Lake excluded. Both residuals display parabolic ($\sim -x^2$) form, with a tendency for under-estimation at low salinities (under about 0.5 S-units), over-estimation in the middle range up to about 1.3 S-units, and underestimation again at high salinities, but this is less extreme with 54 lakes.

As an example of the actual predictive error of the CANOCO models, WA and its variants were performed on the raw datasets NGP1 and NGP2 within CALIBRATE. Table 7.2 demonstrates the behaviour of each model that can be expected outside the dataset, in the form of jackknife estimates of r^2 and RMSE. CANOCO uses 'classical' regression to deshrink estimates according to the equation (ter Braak 1988, Birks *et al.* 1990):

$$initial\ \hat{x}_i = a + bx_i + e_i \qquad (1)$$

which can be rearranged:

$$final\ \hat{x}_i = \frac{(initial\ x_i - a)}{b_i} \qquad (2)$$

Figure 7.2 - Estimated against observed salinity (NGP1 WA)

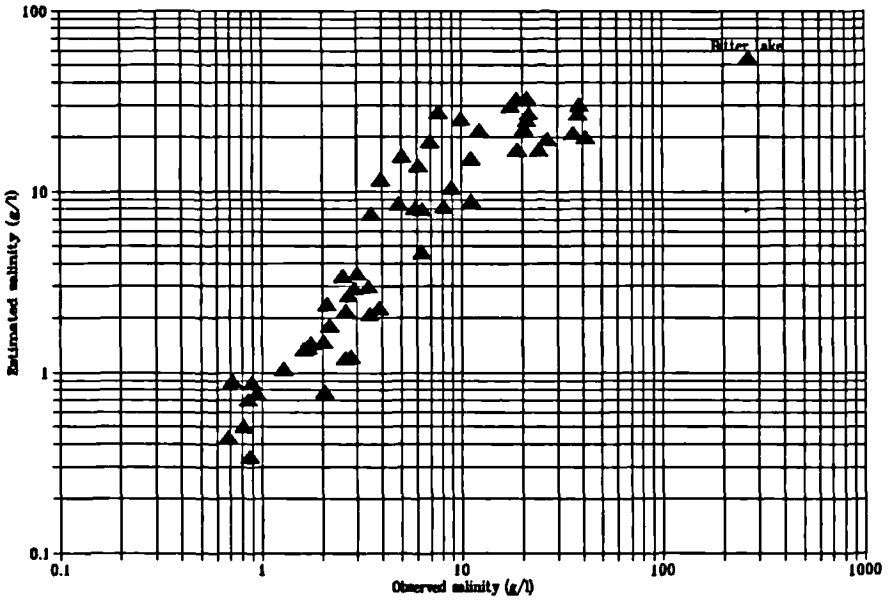


Figure 7.3 - Estimated against observed salinity (NGP2 WA)

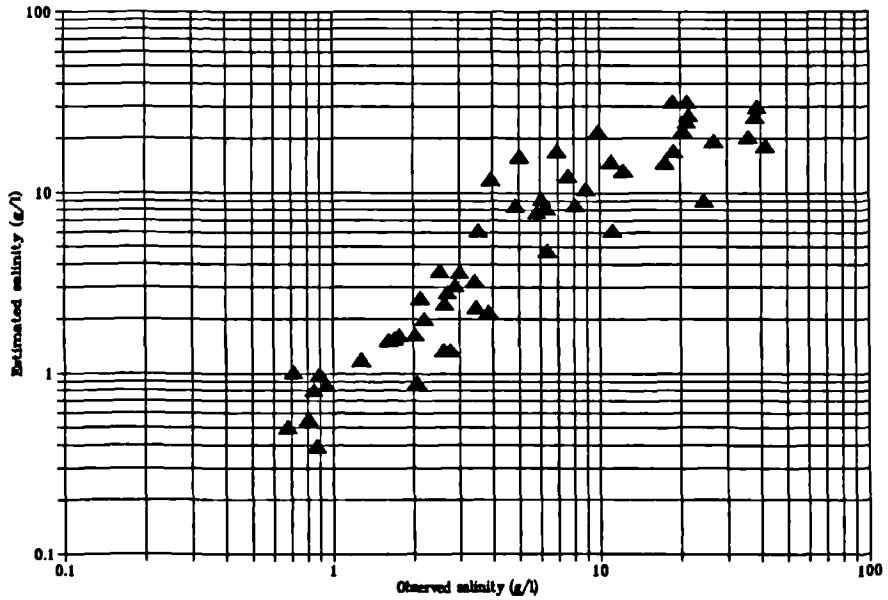


Figure 7.4 : Observed - estimated against observed salinity (NGP1 WA)

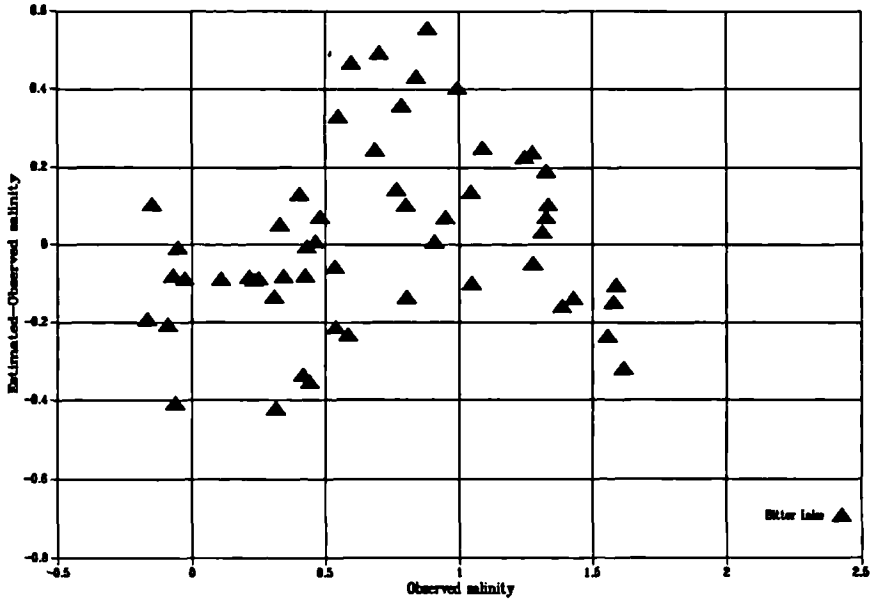
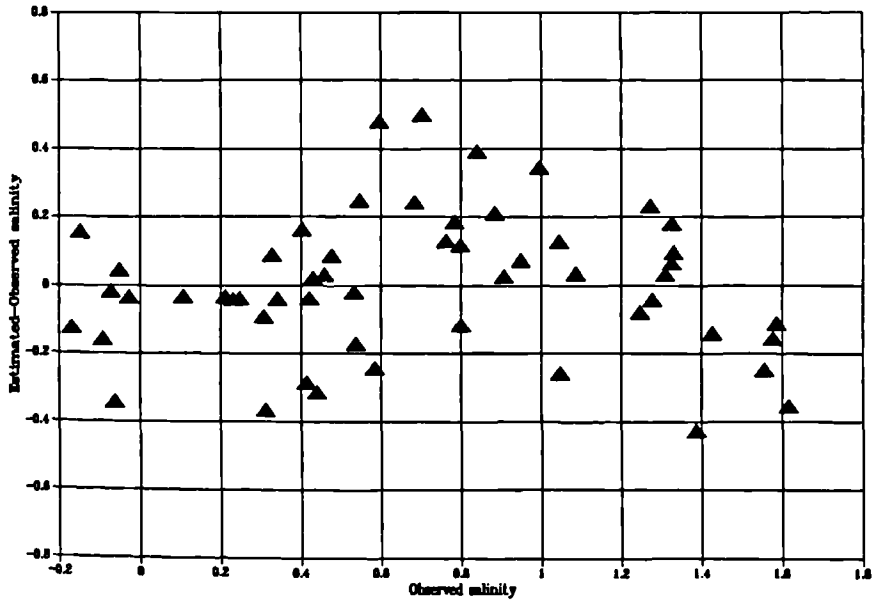


Figure 7.5 : Observed - estimated against observed salinity (NGP2 WA)



Inverse regression is an option within CALIBRATE and tends reduce model RMSE, by deshrinking less than classical methods (Birks *et al.* 1990a). The resulting differences in the methods are demonstrated by table 7.2. The apparent improvement in model performance under tolerance downweighting is confirmed by jackknifing validation in all but one case (NGP1, classical deshrinking). Jackknife validation affirms the goodness-of-fit of the model even with the full 55 lake dataset, though there are considerable improvements when Bitter Lake is removed.

Although the transfer function is improved by using inverse regression in a specific sense, values at the ends of the salinity gradient may lose accuracy compared to classical methods. The best technique to apply to fossil data depends on the known or expected values of salinity likely to be encountered at a site, as each has a domain of values that are most appropriately reconstructed with that method. The best approach to adopt can be decided upon by exploratory analysis with either method in such cases.

7.3.2 Developing weighting systems

Systems of differential species weighting have been applied within the context of WA methods in the form of downweighting rare species as an option within DECORANA (Hill 1979) which was subsequently incorporated into CANOCO (ter Braak 1988). This downweighting option weights the abundance of all taxa with a frequency less than 20% of the most common taxon in proportion to their frequency (Hill 1979, in ter Braak 1988). Downweighting of rare species was not applied during WA calibration within CANOCO as final weights would be a product of all weights applied, rather than reflecting weights based solely on resistance to dissolution.

Transfer functions based on WA methods employ tolerance downweighting in estimating environmental parameters which generally improve calibrations (Chapter 6; table 7.2) with unequal taxon ranges. Additionally, Juggins (1992) further downweighted according to the extent to which taxa are encountered in sediment samples outside their observed live ranges (an index of species transport, I_k) for reconstructing salinity along the tidal River Thames. The combined effect of these weights affected estimated salinity according to the modified equation (from Juggins 1992):

$$\hat{x}_I = \frac{\sum_{k=1}^{m} y_k \hat{u}_k / \hat{t}_k^2 I_k}{\sum_{k=1}^{m} y_k / \hat{t}_k^2 I_k} \qquad (3)$$

The dissolution ranking developed in Chapter 5 formed the basis for a weighting system for both species and samples, and was applied to both the full and reduced NGP datasets (hereafter referred to as NGP1 for the former and NGP2 for the latter, without Bitter Lake). Removal of Bitter Lake did not alter the number of taxa included in NGP2.

The NGP dataset comprises 172 taxa, 10 of which account for 47% of the total abundance in the raw dataset, with *Chaetoceros* cysts alone representing about 10% of total abundance. Fifty taxa could be assigned weights on the basis of dissolution experiments, accounting for about 63.4% of the total (unweighted) species abundance in the dataset. This included some varietal forms whose dissolution behaviour could not be evaluated separately during dissolution experiments (for example, the dissolution rank of *Navicula capitata* is the composite of both varieties encountered, *N. capitata* var *capitata* & var *hungarica*, and both forms in the NGP dataset are treated in the same manner). Conversely, the dissolution ranks of some species split into two taxa during experimental analysis are the average of the separate taxa (such as *Cocconeis placentula* var *euglypta*, var *lineata* & *Co. pediculus* split into raphid and rapheless valves but amalgamated during NGP counting). In the case of the NGP taxon *Cyclotella [quillensis/meneghiniana]*, this taxon was classed according to the average rank of *Cy. meneghiniana* and *Cy. quillensis*. At this stage, other numerically important species not ranked in dissolution experiments were excluded from classification, to restrict the influence on the transfer function to taxa with a known dissolution response (within the confines of the experimental method).

As the object of the weighting approach is to investigate the difference each system has on the outcome of the transfer function as a result of increasing coarseness of classification, the ratio of class numbers is of more significance than the actual divisions chosen, above a certain threshold. For this reason two weighting systems were chosen involving a doubling in the number of classes, set at 10 and 5 classes respectively (DC1 and DC2). The initial choice of ten classes is arbitrary, although the results of other dissolution experiments on diatoms (and other microfossils) covering a range of robustness have suggested that dissolution susceptibility varies over about an order of magnitude (Berger 1968, Parker & Berger 1971, Mikkelsen 1980). The transport index used by Juggins to weight species abundance covers a range of 6 classes (Juggins, 1992), generalised from a much larger range of individual transport values. The approach of reducing variation measured on an interval to an ordinal scale of fewer classes reduces the incorporation of non-significant differences into analysis and expresses a more realistic range of behaviour.

Taxa were assigned to a class on the basis of absolute ***A***-values (Chapter 5), with class 1 containing the most robust and class 10 (or 5) the most susceptible forms (table 7.3). The class

boundaries for DC1 were chosen primarily where visual inspection of the graphs of ***A***-values and the difference of ***A***-values between sequential taxa suggested natural groupings, with the aim to keep similar numbers of taxa in each class where possible. Pairs of dissolution classes were combined to produce the second classification of 5 classes (DC2).

Values for species weighting were derived from these classes directly, and for samples based on a weighted average of constituent species weights. Two alternative approaches of incorporating weights into the transfer function equations were made as a test of the sensitivity of the dataset to the actual form of weighting using each of the two dissolution classifications (DC1 & DC2). The first method (termed here "inverse weighting") uses the dissolution classes to weight species (and samples) by the inverse class number, inverting the scale so that the most resistant taxa have a class of 10 (or 5) and the least resistant class 1.

Dissolution classes can be converted to inverse species weights (ψ_k) by the transformation:

$$\psi_k = \frac{1}{(n_\psi + 1) - C_k} \qquad (4)$$

where ***C*** is the dissolution class of species **k**, and ***n*** the number of classes in each system (10 and 5 respectively for DC1 and DC2). Sample weights (Ψ_i) are calculated analogously, so that:

$$\Psi_i = \frac{1}{(n_\psi + 1) - C_i} \qquad (5)$$

where sample dissolution class (C_i) is a weighted average of species' classes:

$$C_i = \frac{\sum_{k=1}^{m} C_k y_k}{\sum_{k=1}^{m} y_k} \qquad (6)$$

The second technique ("linear weighting") involved weighting species along an arithmetic progression rather than inverse to rank and assumes that there is a constant difference

Table 7.3 - Dissolution classes of 50 NGP taxa (DC1 & DC2)

NGP Code	Taxon	DC1	DC2
MA002B	Mastogloia elliptica var. dansei	1	1
NA024A	Navicula oblonga	1	1
ST006A	Stephanodiscus niagarae	1	1
AN005A	Anomoeoneis costata	2	1
CH9997	Chaetoceros [elmorei/muelleri cysts]	2	1
CP001A	Campylodiscus clypeus	2	1
AM001D	Amphora ovalis var. affinis	3	2
RH001A	Rhopalodia gibba	3	2
SU002A	Surirella ovata	3	2
SU008A	Surirella striatula	3	2
SY005A	Synedra fasciculata	3	2
AM006A	Amphora coffeaeformis	4	2
AM9996	Amphora [cf. coffeaeformis]	4	2
AU003A	Aulacoseira granulata	4	2
AU003B	Aulacoseira granulata var. angustissima	4	2
CM023A	Cymbella pusilla	4	2
CO005A	Cocconeis pediculus	4	2
CY017A	Cyclotella quillensis	4	2
MA001A	Mastogloia smithii	4	2
MA001B	Mastogloia smithii var. lacustris	4	2
CO001B	Cocconeis placentula var. euglypta	5	3
CY012A	Cyclotella caspia	5	3
CY9996	Cyclotella [meneghiniana/quillensis]	5	3
EP004A	Epithemia turgida	5	3
CO001C	Cocconeis placentula var. lineata	6	3
CY003A	Cyclotella meneghiniana	6	3
GO013A	Gomphonema parvulum	6	3
RC001A	Rhoicosphenia curvata	6	3
FR002A	Fragilaria construens	7	4
FR002C	Fragilaria construens var. venter	7	4
FR006A	Fragilaria brevistriata	7	4
FR006B	Fragilaria brevistriata var. inflata	7	4
GM001A	Gomphoneis olivaceum	7	4
NI014A	Nitzschia amphibia	7	4
OP9998	Opephora [cf. olsenii]	7	4
AM001B	Amphora ovalis var. pediculus	8	4
AM003A	Amphora perpusilla	8	4
NA022A	Navicula halophila	8	4
NA022C	Navicula halophila fo. subcapitata	8	4
NA066A	Navicula capitata	8	4
NA066B	Navicula capitata var. hungarica	8	4
NI008A	Nitzschia frustulum	8	4
AC013A	Achnanthes minutissima	9	5
CO006A	Cocconeis diminuta	9	5
DT004B	Diatoma tenue var. elongatum	9	5
NI009A	Nitzschia palea	9	5
NI9996	Nitzschia [cf. palea]	9	5
NI9997	Nitzschia [cf. fonticola]	9	5
FR001A	Fragilaria pinnata	10	5
ST021A	Stephanodiscus minutulus	10	5

between dissolution classes. Inverse weighting gives half the weight to class 9 as class 10, but under a linear progression given a weight of 0.9, and so on in equal tenths to 0.1 (class 1). Both systems weight the highest and lowest classes the same, but differ in the relative weights given to intervening categories.

Linear species weightings (ψ_k) are given by the expression:

$$\psi_k = \frac{C_k}{n_\psi} \qquad (7)$$

Weights for samples (Ψ_i) are derived from the weighted average of species classes:

$$\Psi_i = \frac{\sum_{k=1}^{m} \psi_k \cdot y_{\psi k}}{\sum_{k=1}^{m} y_{\psi k}} \qquad (8)$$

where the sum is only taken over those taxa assigned a class ($\mathbf{y}_{\psi k}$). Values for species and samples range between 0 and 1 under both inverse and linear weighting.

Table 7.3 lists the species allocated dissolution classes, and the resultant species weightings under each system (DC1 and DC2) while table 7.4 gives the sample weightings stemming from these species weights. Despite including the majority of total species abundance in the data, there is considerable variation in the proportion of sample composition that includes classed taxa, and on which sample weight depends. Inevitably some samples have a low proportion of classed taxa, such as Humboldt (16%), Opuntia (17%), Porter (4%), Redberry (17%) and West Stump (20%) These sites are characterised by high proportions of *Stephanodiscus parvus* (NGP2 optimum 2.25 g/l), *Navicula cincta* (optimum 9.3 g/l) or *Nitzschia inconspicua* (optimum 16.5 g/l). A second set of calibrations was carried out on two further datasets excluding these lakes for one system of classification (DC1) under inverse and linear weighting (coded NGP1G-J, NGP2G-J, NGP1g-j & NGP2g-j respectively).

7.3.3 The effects of weighting on WA transfer functions

Weighting species has no effect on the estimated species optima, but is only felt in the

Table 7.4 - Sample weights under linear (L) and inverse (I) weighting

Number	Lake	DC1 (L)	DC1 (I)	DC2 (L)	DC2 (I)	Taxa classed (%)
1	Albert	0.621	0.209	0.638	0.217	47.2
2	Alkaline	0.409	0.145	0.422	0.148	63.3
3	Basin	0.347	0.133	0.376	0.138	75.1
4	Bitter	0.391	0.141	0.392	0.141	100.0
5	Boucher	0.264	0.120	0.269	0.120	37.5
6	Big Quill	0.814	0.349	0.906	0.516	81.7
7	Byron	0.633	0.214	0.636	0.216	71.8
8	Coldwater	0.458	0.156	0.498	0.166	83.0
9	Coon	0.639	0.217	0.670	0.233	28.1
10	Deadmoose	0.606	0.202	0.666	0.231	76.3
11	Devils	0.950	0.668	0.958	0.705	98.6
12	Eckelson	0.382	0.139	0.386	0.140	30.9
13	East Coteau	0.790	0.323	0.867	0.428	91.4
14	East Devils	0.410	0.145	0.442	0.152	90.2
15	Elbow	0.435	0.150	0.490	0.164	61.3
16	Fife	0.720	0.263	0.726	0.267	80.9
17	Fishing	0.548	0.181	0.612	0.205	77.2
18	Free People	0.440	0.152	0.450	0.154	92.5
19	George	0.318	0.128	0.369	0.137	96.2
20	Hazelden	0.238	0.116	0.245	0.117	72.8
21	Herman	0.486	0.163	0.528	0.175	86.5
22	Hoseshoe	0.488	0.163	0.522	0.173	48.6
23	Humboldt	0.483	0.162	0.574	0.190	15.5
24	Isabel	0.310	0.127	0.355	0.134	87.8
25	Lenore	0.642	0.218	0.728	0.269	68.6
26	Long	0.418	0.147	0.474	0.160	72.1
27	Madison	0.498	0.166	0.544	0.180	48.7
28	Medicine	0.540	0.179	0.586	0.195	60.4
29	Mission Bay	0.396	0.142	0.410	0.145	91.7
30	Moon	0.466	0.158	0.497	0.166	83.7
31	Norden	0.632	0.214	0.655	0.224	49.6
32	Oakwood	0.506	0.168	0.550	0.182	37.0
33	Opuntia	0.663	0.229	0.686	0.241	16.8
34	Piyas	0.320	0.128	0.332	0.130	46.3
35	Poinsett	0.318	0.128	0.367	0.136	30.9
36	Porter	0.619	0.208	0.695	0.247	3.8
37	Rabbit	0.446	0.153	0.469	0.159	97.8
38	Redberry	0.546	0.181	0.604	0.202	17.2
39	Reflex	0.565	0.187	0.629	0.212	47.1
40	Roslyn	0.584	0.194	0.606	0.202	41.0
41	Round, Benson	0.795	0.328	0.807	0.341	36.1
42	Round, McHenr	0.666	0.230	0.727	0.268	46.5
43	Roy	0.460	0.156	0.512	0.170	37.3
44	Sayer	0.466	0.158	0.482	0.162	39.4
45	Shinbone	0.265	0.120	0.286	0.123	74.0
46	Spring	0.287	0.123	0.309	0.126	80.4
47	Spiritwood	0.541	0.179	0.577	0.191	44.3
48	Stink, Stutsman	0.298	0.125	0.325	0.129	56.9
49	Stink, Benson C	0.361	0.135	0.379	0.139	87.0
50	Tramping	0.502	0.167	0.515	0.171	84.2
51	Twin	0.593	0.197	0.639	0.217	61.0
52	Wakaw	0.535	0.177	0.581	0.193	48.8
53	Waldsea	0.550	0.182	0.594	0.197	77.7
54	Waubay	0.372	0.137	0.389	0.141	82.1
55	West Stump	0.381	0.139	0.400	0.143	20.5

reconstructed environmental parameter:

$$\hat{u}_{k\psi} = \frac{\sum_{i=1}^{n} (y_i \cdot \psi_k)\, x_i}{\sum_{i=1}^{n} (y_i \cdot \psi_k)} = \hat{u}_k \qquad (9)$$

as ψ_k is a constant for any species over all sites. The estimate of the environmental parameter is a weighted form of the classical WA estimate:

$$\hat{x}_{\psi i} = \frac{\sum_{k=1}^{m} (y_k \cdot \psi_k)\, \hat{u}_k}{\sum_{k=1}^{m} (y_k \cdot \psi_k)} \qquad (10)$$

Weighting samples alone affects environmental estimates by virtue of the effect on species optima (as can be seen in the case of Bitter Lake, effectively given a weight of 0 by exclusion):

$$\hat{u}_{k\Psi} = \frac{\sum_{i=1}^{n} (y_i \cdot \Psi_i)\, x_i}{\sum_{i=1}^{n} (y_i \cdot \Psi_i)} \qquad (11)$$

as the sum is made over all samples for each species. Site scores are unaffected by site weighting in itself, in a similar manner to that for species optima under species weighting, as the sum is over all taxa at a site with a constant downweight:

$$\hat{x}_{\Psi i} = \frac{\sum_{k=1}^{m} (y_k \cdot \Psi_i)\, \hat{u}_{k\Psi}}{\sum_{k=1}^{m} (y_k \cdot \Psi_i)} = \frac{\sum_{k=1}^{m} y_k \hat{u}_{k\Psi}}{\sum_{k=1}^{m} y_k} \qquad (12)$$

Weighting both species and sites has a compound effect on final environmental estimates as

species optima are affected by site weights, and species weighting additionally gives different weights to these in the estimate:

$$\hat{u}_{k\psi\Psi} = \frac{\sum_{i=1}^{n} (y_i \cdot \psi_k \cdot \Psi_i) x_i}{\sum_{i=1}^{n} (y_i \cdot \psi_k \cdot \Psi_i)} = \hat{u}_{k\Psi} \qquad (13)$$

Environmental estimates are given by:

$$\hat{x}_{\psi\Psi i} = \frac{\sum_{k=1}^{m} (y_k \cdot \psi_k \cdot \Psi_i) \hat{u}_{k\Psi}}{\sum_{k=1}^{m} (y_k \cdot \psi_k \cdot \Psi_i)} \qquad (14)$$

which simplifies to:

$$\hat{x}_{\psi\Psi i} = \frac{\sum_{k=1}^{m} (y_k \cdot \psi_k) \hat{u}_{k\Psi}}{\sum_{k=1}^{m} (y_k \cdot \psi_k)} \qquad (15)$$

Each calibration trial consisted of running CANOCO with manual input of weights for each of three combinations, testing the effects of weighting species and samples separately, and both species and samples together. In each case the control was provided by running an unweighted calibration of the relevant dataset. These are coded according to dataset used (NGP1 or NGP2), component weighted, and system of classification used (DC1 or DC2), as shown in tables 7.5 & 7.6. Inverse weighting is differentiated from linear by the use of capitalisation of codes for the inverse method. The trials coded **g**, **h**, **i** and **j** (or **G**, **H**, **I** and **J**) relate to reduced datasets, with 5 lakes removed (see section 7.3.2).

7.3.4 Results

Weighting in any form improves the transfer function with respect to model regression r^2 values with minor reductions in RMSE under many conditions (table 7.5 & 7.6), although the actual prediction errors are likely to be larger. In terms of r^2 values, inverse (table 7.5) and linear (table 7.6) weighting perform comparably, linear weighting achieving slightly better results with NGP2,

Table 7.5 - Model results under inverse weighting

Code	Weighting		Sample outliers		$\%\lambda_1$	λ_1/λ_2	r	RMSE
	Type	DC	Lake	Leverage				
NGP1	None	—	Bitter	6.3	4.5	0.816	0.913	0.245
NGP1A	1 & 2	DC1	—	—	4.0	0.749	0.924	0.230
NGP1B	1	DC1	Bitter	5.1	4.5	0.756	0.918	0.240
NGP1C	2	DC1	—	—	4.0	0.832	0.923	0.228
NGP1D	1 & 2	DC2	Big Quill	7.9	4.2	0.749	0.921	0.230
NGP1E	1	DC2	Big Quill	5.1	4.5	0.743	0.917	0.237
NGP1F	2	DC2	—	—	4.1	0.853	0.923	0.228
NGP1G	None	—	Bitter	6.0	4.8	0.882	0.922	0.228
NGP1H	1 & 2	DC1	Big Quill	5.1	4.3	0.777	0.943	0.226
NGP1I	1	DC1	—	—	4.9	0.774	0.928	0.233
NGP1J	2	DC1	—	—	4.2	0.857	0.940	0.223
NGP2	None	—	—	—	4.7	0.910	0.926	0.206
NGP2A	1 & 2	DC1	—	—	4.1	0.758	0.926	0.204
NGP2B	1	DC1	—	—	4.7	0.788	0.930	0.201
NGP2C	2	DC1	—	—	4.0	0.844	0.924	0.204
NGP2D	1 & 2	DC2	Big Quill	8.4	4.3	0.762	0.924	0.203
NGP2E	1	DC2	Big Quill	6.0	4.7	0.774	0.930	0.201
NGP2F	2	DC2	—	—	4.2	0.869	0.926	0.202
NGP2G	None	—	—	—	5.1	0.934	0.937	0.198
NGP2H	1 & 2	DC1	Big Quill	5.3	4.4	0.785	0.946	0.197
NGP2I	1	DC1	—	—	5.1	0.808	0.942	0.190
NGP2J	2	DC1	—	—	4.3	0.871	0.942	0.195

Weighting type is coded as follows: 1 - Samples; 2 - Species; 1 & 2 - Samples & species

Table 7.6 - Model results under linear weighting

Code	Weighting		Sample outliers		$\%\lambda_1$	λ_1/λ_2	r	RMSE
	Type	DC	Lake	Leverage				
NGP1	None	—	Bitter	6.3	4.5	0.816	0.913	0.245
NGP1a	1 & 2	DC1	—	—	4.2	0.823	0.924	0.233
NGP1b	1	DC1	Bitter	5.2	4.6	0.835	0.919	0.241
NGP1c	2	DC1	—	—	4.1	0.861	0.922	0.231
NGP1d	1 & 2	DC2	—	—	4.3	0.834	0.924	0.232
NGP1e	1	DC2	—	—	4.6	0.841	0.919	0.240
NGP1f	2	DC2	—	—	4.1	0.865	0.923	0.229
NGP1g	None	—	Bitter	6.0	4.8	0.882	0.922	0.228
NGP1h	1 & 2	DC1	—	—	4.6	0.848	0.939	0.234
NGP1i	1	DC1	Bitter	5.1	5.0	0.853	0.930	0.224
NGP1j	2	DC1	—	—	4.4	0.881	0.935	0.238
NGP2	None	—	—	—	4.7	0.910	0.926	0.206
NGP2a	1 & 2	DC1	—	—	4.3	0.840	0.928	0.207
NGP2b	1	DC1	—	—	4.8	0.871	0.931	0.203
NGP2c	2	DC1	—	—	4.2	0.880	0.927	0.203
NGP2d	1 & 2	DC2	Big Quill	5.2	4.4	0.851	0.928	0.206
NGP2e	1	DC2	—	—	4.8	0.877	0.931	0.202
NGP2f	2	DC2	—	—	4.3	0.884	0.927	0.203
NGP2g	None	—	—	—	5.1	0.934	0.937	0.198
NGP2h	1 & 2	DC1	Big Quill	5.0	4.7	0.867	0.944	0.191
NGP2i	1	DC1	—	—	5.2	0.894	0.944	0.192
NGP2j	2	DC1	—	—	4.6	0.904	0.941	0.192

Weighting type is coded as follows: 1 - Samples; 2 - Species; 1 & 2 - Samples & species

but very similar with NGP1, datasets. There is little difference between the two classification systems on the models, DC1 performing marginally better with inverse weighting than DC2, particularly using the full data (NGP1A-C compared to NGP1D-F, table 7.5). The best models were consistently those based on the smallest lake dataset (NGP1G-J and NGP1g-j, with 50 lakes, and NGP2G-J and NGP2g-j, with 49 lakes), as might be expected.

Table 7.5 & 7.6 also include samples with high leverage (ter Braak, 1990) in terms of extreme salinity values (as weighted mean). The behaviour of samples under different strategies is interesting. For example, Bitter Lake ceases to be a conspicuous (statistical) outlier under linear weighting by species and samples (NGP1a, NGPd and NGP1h; table 7.6). Under inverse weighting with DC2, Big Quill is noticeable as a univariate outlier (NGP1D & E, NGP2D & E; table 7.5). With linear weighting four models have samples shown as extreme (table 7.6), while this occurs in seven calibrations with inverse weighting (table 7.5).

Both weighting systems (inverse and linear) improve the unadjusted models, and perform similarly, differing in detail as different samples exert more or less influence on the model, depending on the precise weighting regime. The ratios of the first to second axes (λ_1/λ_2) are generally higher for linear than inverse weighting, but all first axes are significant at p=0.01 (Monte Carlo test, 99 permutations). In all cases, treating Bitter Lake as a rogue and removing it improved the results, as the salinity of this site is always underestimated from its apparent species data.

As expected, there is a correlation between r^2 and RMSE for any particular model, an increase in the former tending to lead to a decrease in the latter (figure 7.6). The split between NGP1 and NGP2 datasets is clear, but choosing the "best" model from this set for salinity reconstruction of any particular fossil sample is best achieved by graphical examination of the predicted and observed performance under each, as the accuracy of the transfer function is not equal across all salinity values. Figures 7.7-7.12 show the predicted against observed salinities for all NGP models. The residual structure of all models is similar to their controls (NGP2 and NGP2g), tending to underestimate at the extremes and overestimate in a middle range, though this is more apparent with any dataset including Bitter Lake (figures 7.7-7.12, compared to figure 7.2).

As not all taxa could be assigned to a dissolution class, the effect is to increase the proportion of other taxa (given a weight of 1 by default). After weighting 50 taxa, the proportion of unweighted taxa increased to over 50% of the total species abundance in the dataset. A further 11 taxa were classed according to the most similar known taxa, based on gross valve

Figure 7.6 : RMSE against r^2 (all WA models)

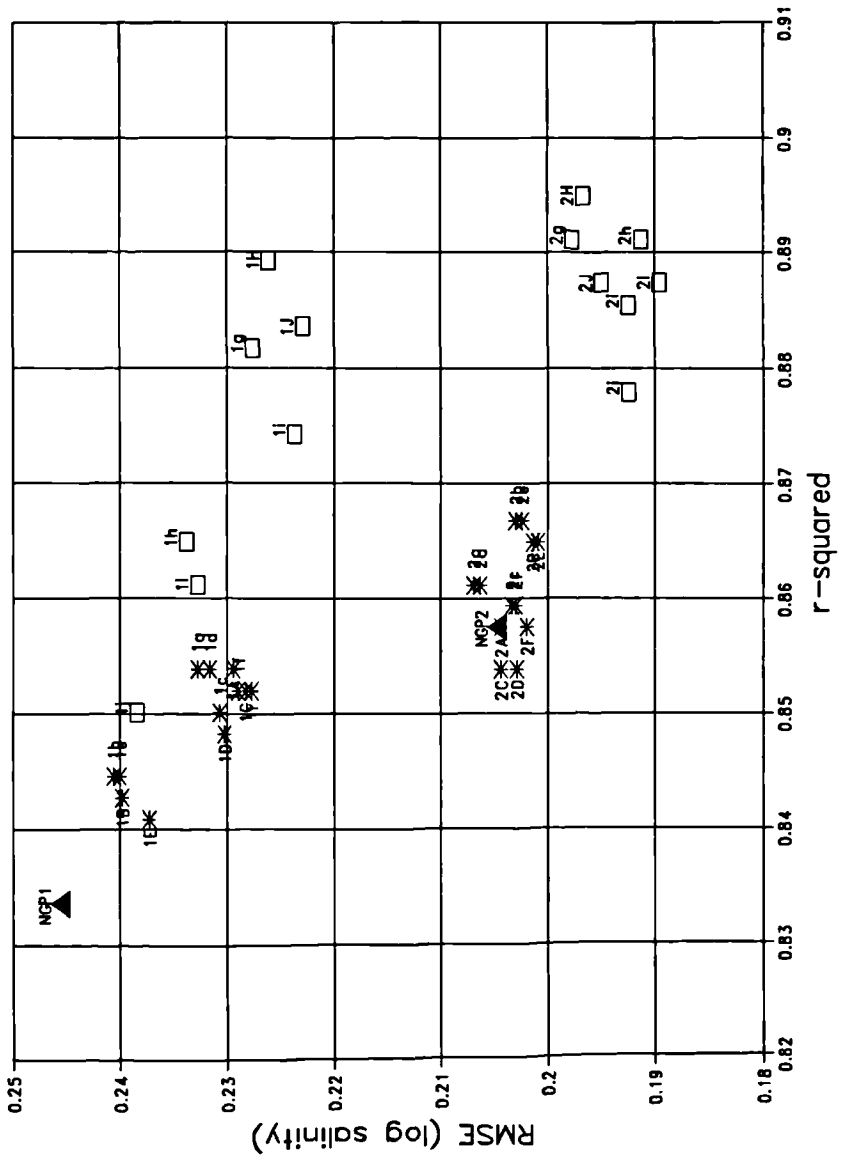


Figure 7.7 : Estimated against observed salinity (NGP2A-C WA)

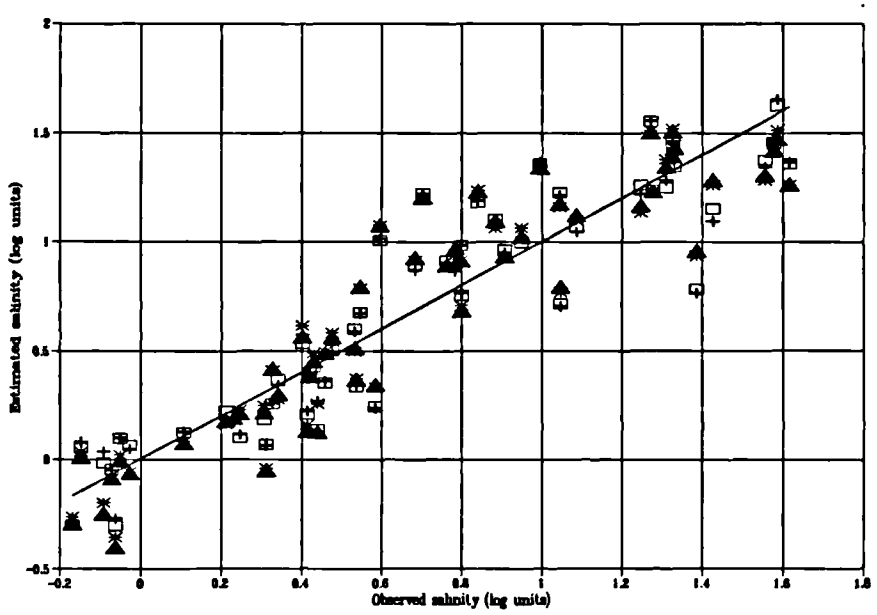
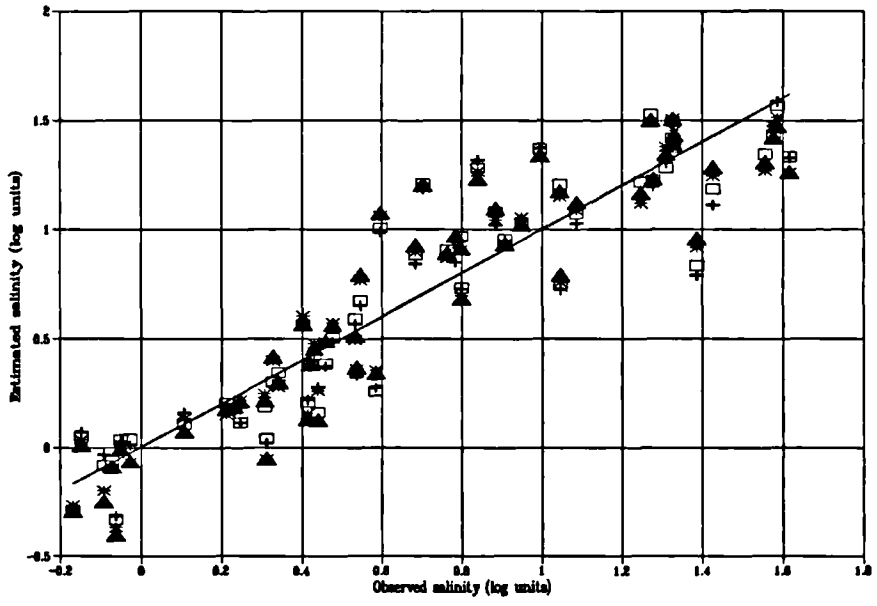


Figure 7.8 : Estimated against observed salinity (NGP2D-F WA)



▲ : Unweighted control; + : sample & species weighting; * : sample weighting;
□ : species weighting

Figure 7.9 : Estimated against observed salinity (NGP2G-J WA)

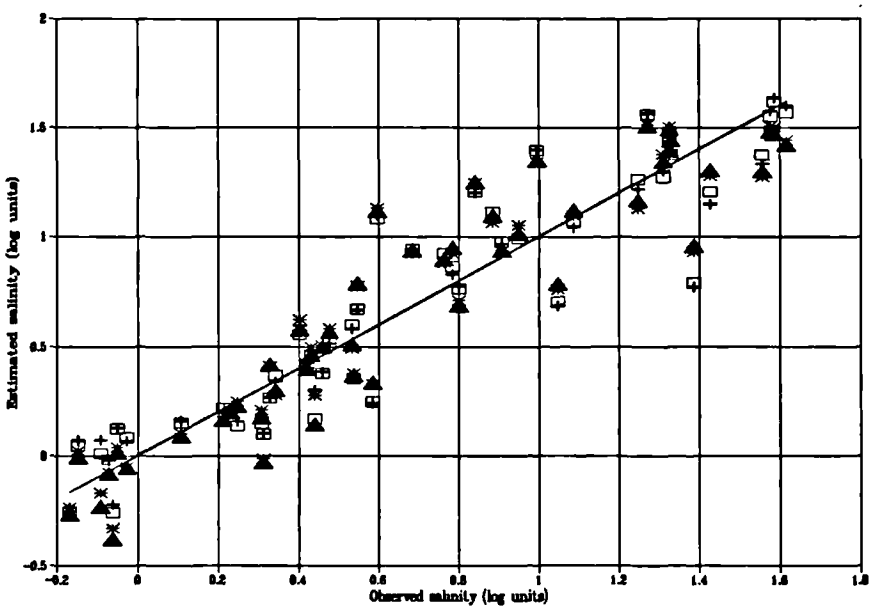
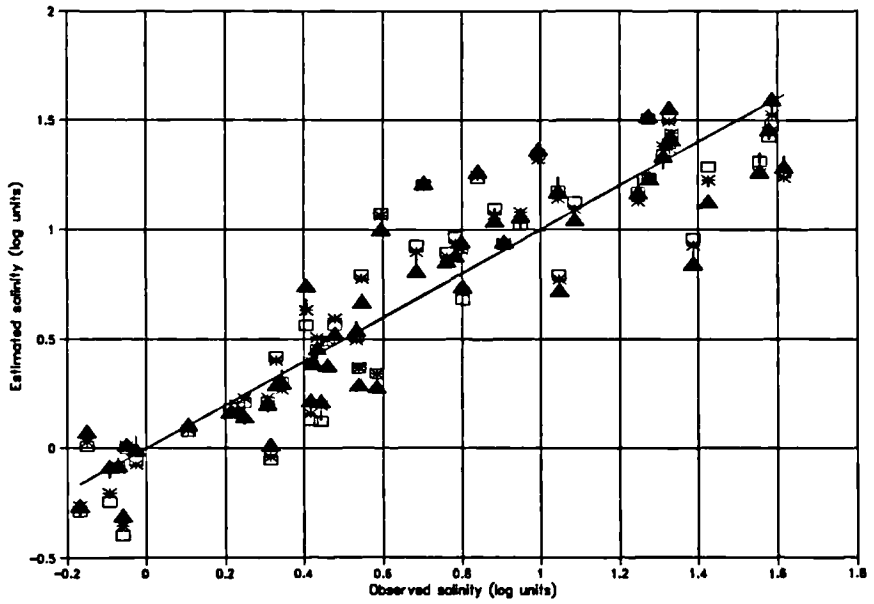


Figure 7.10 : Estimated against observed salinity (NGP2a-c WA)



▲ : Unweighted control; + : sample & species weighting; * : sample weighting;
□ : species weighting

Figure 7.11 : Estimated against observed salinity (NGP2d-f WA)

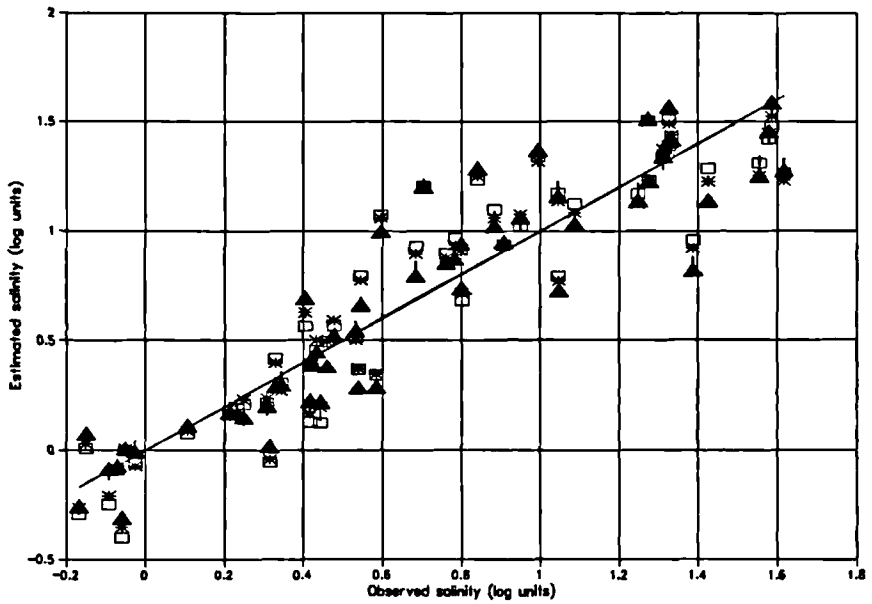
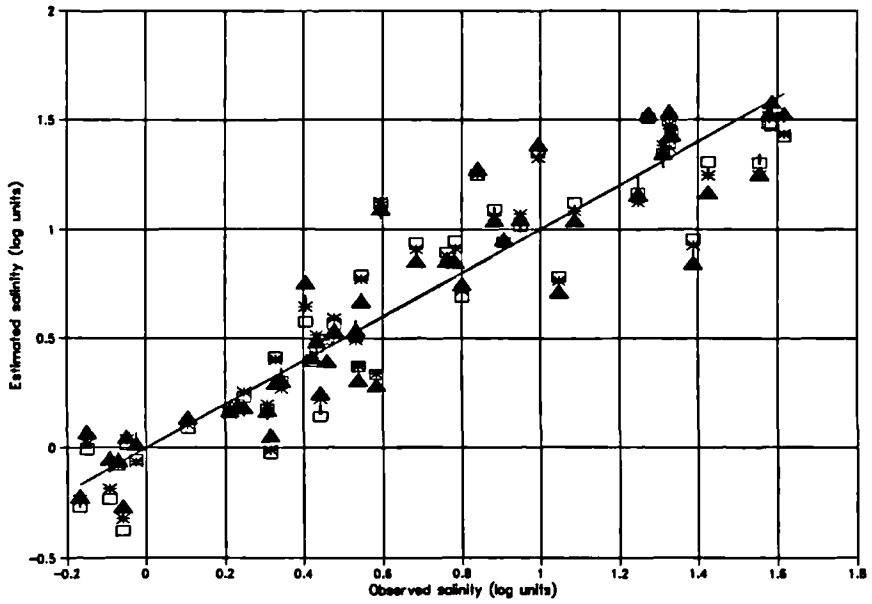


Figure 7.12 : Estimated against observed salinity (NGP2g-j WA)



▲ : Unweighted control; + : sample & species weighting; * : sample weighting;
□ : species weighting

morphology (table 7.7). Preliminary results using species weighting only, suggested that, although over 76% of taxa were then included in the calibration, the correlation (in terms of r^2) was lowered, compared to the original 50 taxa classed, under both DC1 and DC2, and with inverse and linear weighting (table 7.8). Incorrect classification may reduce the model improvement, and morphological similarity is not necessarily a good guide to dissolution behaviour (Lawson *et al.* 1978).

7.3.5 Application to Spiritwood short core

Three calibrations using linear weighting of NGP2 data were chosen to reconstruct salinity from 18 samples spanning the last 150 years at Spiritwood Lake, using species weighting alone (NGP2c,f,j). These appeared to provide the best estimates at lower salinities (less than about 5g/l; figures 7.7-7.12) compared to a reconstruction with the control model NGP2. Passive samples within CANOCO are linked to active samples on the basis of common taxa, which in the case of the Spiritwood samples include over 95% of the species sum. Computed sample scores along the canonical axis can be converted to salinity outside CANOCO by using the formula (ter Braak 1988):

$$\hat{z}_{i1} = \overline{z_1} + \frac{\sigma_1 \cdot x_1}{c_1} \qquad (16)$$

where:

- z_1 and σ_1 are the mean and standard deviation of the calibration variable (salinity, $\log_{10}$ units)
- x_1 is the sample score on the first axis
- c_1 is the canonical coefficient of the standardised calibration variable

These salinity reconstructions are examined in more detail below.

7.3.6 Improvement of the transfer function

Dissolution is only one of several problems affecting environmental inference from saline lake diatom assemblages. The wide tolerance of *Chaetoceros elmorei/muelleri* may be the artificial consequence of taxonomic difficulty in differentiating between taxa which are found only as resting spores or cysts in sediments (Fritz *et al.* 1993) which corresponds to the extreme susceptibility of the uncysted form from dissolution experiments (Chapter 5). Problems exist amongst certain key genera, including *Amphora* (for example *A. coffeaeformis* and *A. acutiuscula*), *Nitzschia* (notably the *N. frustulum* and *N. fonticola* group), *Stephanodiscus* and

Table 7.7 - Dissolution classification of 11 additional taxa

NGP Code	Taxon	DC1	DC2
AM002A	*Amphora acutiuscula*	4	2
AM001A	*Amphora ovalis*	1	1
AU002A	*Aulacoseira ambigua*	4	2
CO001A	*Cocconeis placentula*	5	3
CC001A	*Cyclostephanos dubius*	8	4
NI043A	*Nitzschia inconspicua*	9	5
ST001A	*Stephanodiscus hantzschii*	10	5
ST010A	*Stephanodiscus parvus*	10	5
ST9988	*Stephanodiscus parvus/hantzschii*	10	5
SU002C	*Surirella ovata* var *crumena*	3	2
SU011A	*Surirella peisonis*	3	2

Table 7.8 - Model results (61 classed taxa; species weighting)

Data set	Species weighting		Sample outliers		$\%\lambda_1$	λ_1/λ_2	r
	Type	DC	Lake	Leverage			
NGP1	None	—	Bitter	6.3	4.5	0.816	0.913
	Inverse	DC1	—	—	4.0	0.812	0.920
	Linear	DC1	—	—	4.2	0.817	0.919
	Inverse	DC2	—	—	4.2	0.835	0.919
	Linear	DC2	—	—	4.2	0.828	0.919
NGP2	None	—	—	—	4.7	0.910	0.926
	Inverse	DC1	—	—	4.1	0.823	0.922
	Linear	DC1	—	—	4.3	0.833	0.922
	Inverse	DC2	—	—	4.3	0.845	0.921
	Linear	DC2	—	—	4.4	0.843	0.923

Cyclotella (for instance the *C. quillensis/meneghiniana* division), which are important components of the species data with often distinct ecological niches. A recent re-evaluation of *Cyclotella caspia* itself has suggested that all of the NGP material may be *C. choctawhatcheeana* (Dr. Lawrence Carvalho, pers. comm.). While a single renaming does not affect the transfer function, differences can be expected if several ecologically distinct species have been included under one taxonomic name (such as *Chaetoceros* cysts and within the *Nitzschia frustulum/fonticola* group, Fritz *et al.* 1993). It is likely that as more taxonomic uncertainties are resolved, a better understanding of diatom ecology and distribution will emerge. If this is to lead to improvements in the transfer function, recounting of the surface sediment training set may be necessary.

The linkage of diatom distribution to salinity (or other variables) depends on how representative the sediment assemblage is of the measured environmental parameters (not considering taphonomic alteration). For many closed basins, salinity is highly variable both within and between years (Hammer 1986, Last 1983), and taxa which bloom in spring or autumn may not have an optima adequately estimated by a mid-summer sample, or an average of seasonal samples. Surface sediments in the NGP dataset, using the top 3cm, represent 2-5 years of accumulation (Fritz *et al.* 1993). Species composition may be the result of a range of salinities, from reworked sediments, with different lengths of exposure to taphonomic processes. These processes may continue in the laboratory, as vigorous preparation techniques may exacerbate natural breakage and dissolution.

Weighting species and samples according to dissolution ranks is an ad-hoc approach to the more fundamental problem of sample preservation. The implicit assumption is that robust species will be over-represented in dissolved samples, and hence the proportion of robust taxa in a sample is a measure, however rough, of sample dissolution. It is this attribute that is the most important in determining how the transfer function operates, as species weighting does not alter a taxon's estimated optimum under WA. Many studies have used the presence, or proportion, of robust and susceptible taxa, as indicative of dissolution (*e.g.* Ruddiman & Heezen 1967, Berger 1968, Parker & Berger 1971, Johnson 1974, Thunell 1976, Peterson & Prell 1985, Shemesh *et al.* 1989), which is a useful estimate in many situations.

The improvements in the results of transfer functions using weightings, even of a partial species set, lend support to this technique, but cannot provide the best solution. Perfectly preserved samples should be given full weight, regardless of the taxa present, as these are reflecting true (death) assemblages from which ecologically valid conclusions can be drawn. Equally, badly preserved samples should be downweighted, as a reflection of the quality of data that sample represents, and the confidence that can be invested in it. The approach will provide better

estimates in those situations where well preserved samples are dominated by more susceptible taxa, and badly preserved samples contain robust taxa, but provide inappropriate weightings in different circumstances. Complications arise where diatom communities do not contain a range of susceptibilities, as a result of other limnological factors, such as type and availability of habitat, or control by other biotic and abiotic conditions.

If the distribution of robust or fragile forms was equal (as a proportion of species diversity) across all salinities, dissolution would be recorded as an increase in robust proportions at all sites, and weighting based on species resistance could theoretically account for this under a suitable weighting system. This would hold under all conditions of dissolution, however distributed across sites, with the important proviso that reconstructions would always be imperfect as information is lost as each taxon disappears from the sedimentary record. Figures 7.13a & b shows the relationship of dissolution classes (DC1 & DC2) with respect to salinity optima (NGP2 WA estimates). There is no obvious bias in the distribution of susceptible or robust taxa with salinity (although the salinity optima estimates have already been affected by varying degrees of dissolution of surface sediment samples).

Stage-counting samples is a means of objectively assessing sample preservation, deciding on a minimum level for inclusion in a calibration dataset, and setting up a classification system in a similar way as that based on species ranks. Blanket exclusion of dissolved samples from the calibration set is not a realistic option, and undesirable given the range of dissolution that can be expected in fossil samples, and the inaccuracy that this inequality causes in reconstructions (Hutson 1977). Samples can be screened on the evidence of actual dissolution state, rather than proxies based on the dissolution rank of constituent species.

Downweighting samples cannot in itself be expected to recover the optimum of a susceptible taxon, if dissolution (and resultant downweighting) is asymmetric about its true optimum. A compound approach would be to recalculate species' proportions within dissolved samples before WA calibration, based on the ranks of constituent taxa, or the dissolution index/population relationships (where known) of individual taxa. Knowledge of dissolution indices of each taxon in a sample provides a basis for excluding certain taxa from the count, in the case of obviously reworked valves, or at least those that cannot be assumed representative of the environmental data collected at the time. This approach could also be applied to passive samples which cannot be adjusted for sample dissolution within WA calibration.

Where the dissolution behaviour of a taxon is not known, comparison to similar morphotypes may not be an accurate guide. Performance of the transfer function may be improved by

Figure 7.13a : Taxon salinity optima (NGP2 WA) against dissolution class (DC1)

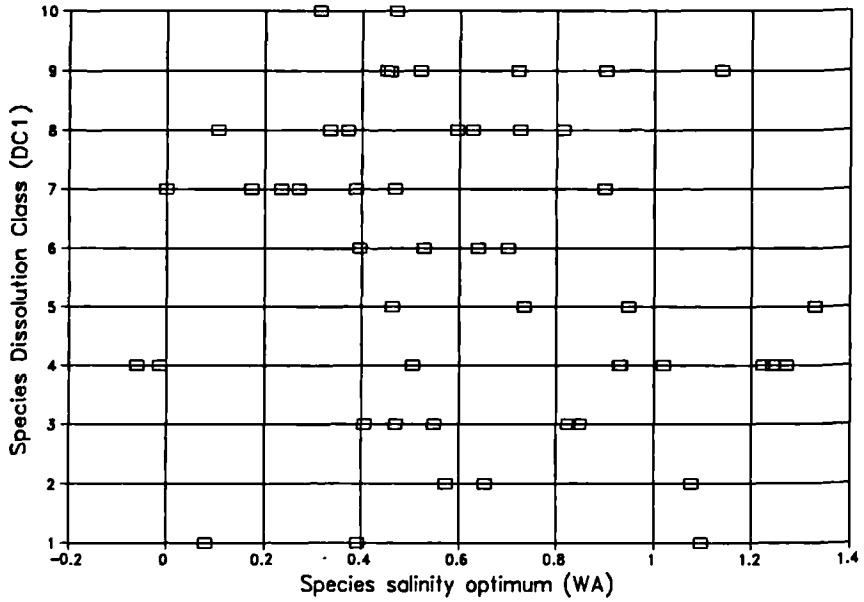
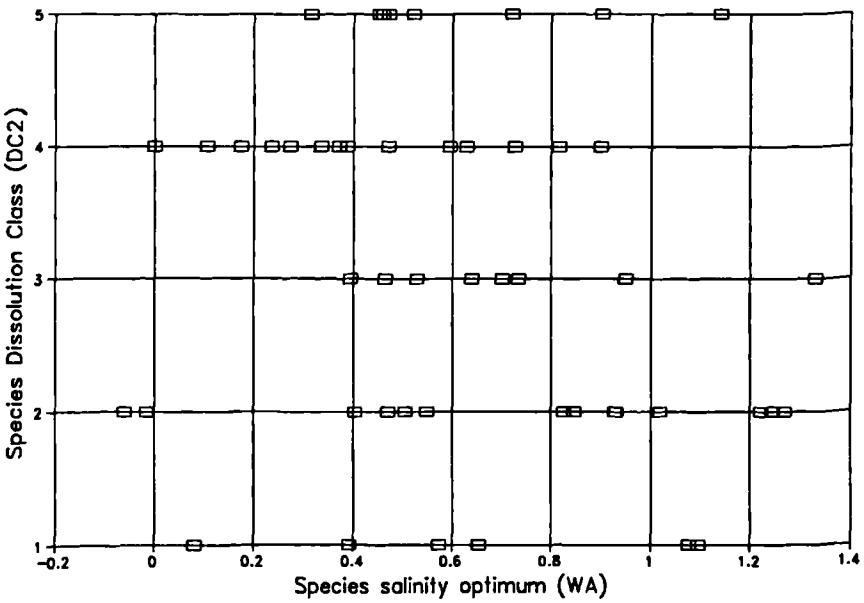


Figure 7.13b : Taxon salinity optima (NGP2 WA) against dissolution class (DC2)



excluding samples with high percentages of "unknown" taxa from calibration, if this does not imbalance the training set. Alternatively, some unknown taxon could be removed from the training set and the species composition recalculated for each sample. It is encouraging that the transfer function performed better despite unclassified species, and may improve further if more taxa can be reliably assigned a class on the basis of experiment.

Dissolution indices can also provide a qualitative measure of confidence for reconstructed parameters, in addition to flagging samples lacking close analogues with the calibration dataset, and those with a poor fit to the constrained variable (Birks *et al.* 1990).

7.4 Recent environmental change at Spiritwood Lake

7.4.1 Introduction

A short core was taken from Spiritwood Lake in August 1991 as a test for the effect of incorporating dissolution rank weighting on the salinity transfer function. This core (SW1, 82 cm) was recovered from 13.4 m provides a record of change from a period before European settlement in the region. Radiometric dating based on ^{210}Pb analysis under the constant rate of supply hypothesis (Appleby & Oldfield 1978; Appleby *et al.* 1986), additionally supported by ^{137}Cs and ^{241}Am peaks defining the early 1960s, suggests that the core represents about 150 years of accumulation to about 60 cm (the lowest dateable horizon by this method).

The core was sectioned in 1 cm intervals for the top 30 cm, and then in 2cm slices until the bottom. Every sample was analysed for organic content (by loss-on-ignition at 550°C) and carbonate content (subsequent weight loss at 950°C) and eighteen samples were analysed for diatoms. Counts were made of 400-500 valves from each sample, using dissolution stage methods. These samples were passively included in CANOCO calibrations using four different models (see above) for reconstructions of salinity over the last 140 years.

7.4.2 The Spiritwood Lake restoration scheme

Spiritwood Lake has been recognised as being subject to severe eutrophication since the mid-1970s (Sauer 1987) primarily as a result of non-point sources of nitrogen and phosphorous. Since 1980, Spiritwood Lake has been the focus for a novel "restoration" project, implemented by the North Dakota State Department of Health, which has combined catchment management and more importantly direct pumping of hypolimnetic bottom water during stratification. Pumping of hypolimnetic water takes place one or two months before spring turnover and after the late summer algal bloom until the second turnover, generally mid-June to mid-September (Sauer

1988), subject to lake elevation. Water was removed every year from 1982 to 1988, with the exception of 1985, and over 1000 acre-feet were pumped out in 1983, 1984 and 1987. A nearby dry lake (Schock Lake) acts as a receiving wetland. Over this period, some 76,000 pounds of nitrogen (as total Kjeldahl nitrogen, TKN) and 6,000 lbs of phosphorous (as total phosphorous, TP) have been extracted, in 4,330 acre-feet of lake water.

Figures 7.14-7.17 present the data concerning changes in lake level, and TDS, NO_3-N and PO_4-P (at 0.5m depth) over this time (redrawn from data in Sauer 1988). Apart from some isolated measurements, limited limnological information before 1980 prevents unequivocal conclusions as to the role of pumping in the changes observed (pumping periods indicated by solid bars), and only contiguous monthly measurements have been linked on the diagrams. Lake levels appear to respond to downdrawing as well as summer evapotranspiration, inputs from spring thaw and more unpredictable and extreme rainfall events (for example that of May 1986, a rainstorm with an estimated return period over 25 years; Sauer 1988). Nitrogen and particularly phosphorous levels appear to have been reduced, at least in terms of variability, the latter which is attributed to the control of sediment input from the catchment. Nitrogen is considered to be a limiting nutrient, often reaching trace concentrations in surface waters during summer months (figure 7.17). Spiritwood Lake would still be classed as eutrophic under OECD guidelines (0.04-0.1 mg/l TP), but the scheme can claim some success in the reduction of hypertrophy (>0.1 mg/l TP; OECD 1982, in Bennion 1994).

The effects on the non-diatom community have been significant, with reported blooms of large-bodied *Daphnia* at depth, a decline in the abundance and diversity of cyanophyta (essentially *Lyngba spp.*), an increase in chlorophytes (*Scenedesmus spp*, *Pediastrum spp.* and *Chlorella spp.*) and a delay and reduction in the spring diatom bloom (Sauer 1988). It is not possible from the available data to establish any consistent relationship between lake level and TDS, unlike other closed lakes in the region, noticeably Devil's Lake, before pumping occurred, but from the measurements since 1982, any such relationship has been decoupled at Spiritwood Lake.

7.4.3 Physical analysis

Figure 7.18 shows the variation in organic content and carbonate content (as CO_3^{2-}) as a percentage of dry weight for the core. Organic content has always been relatively high, and if anything suggests a decrease in content over the last 150 years. On a smaller scale, there are peaks at the start of European settlement (at the lake, about 1880; Johnson 1950) as well as one predating this. Apparent variability from the late 1940s coincides with the increase in resolution of sampling (30cms), although this increased resolution reveals a sudden drop in the mid to late 1980s, which may be related to lake management practises implemented about this

Figure 7.14 - Spiritwood Lake Elevation, 1982-1988

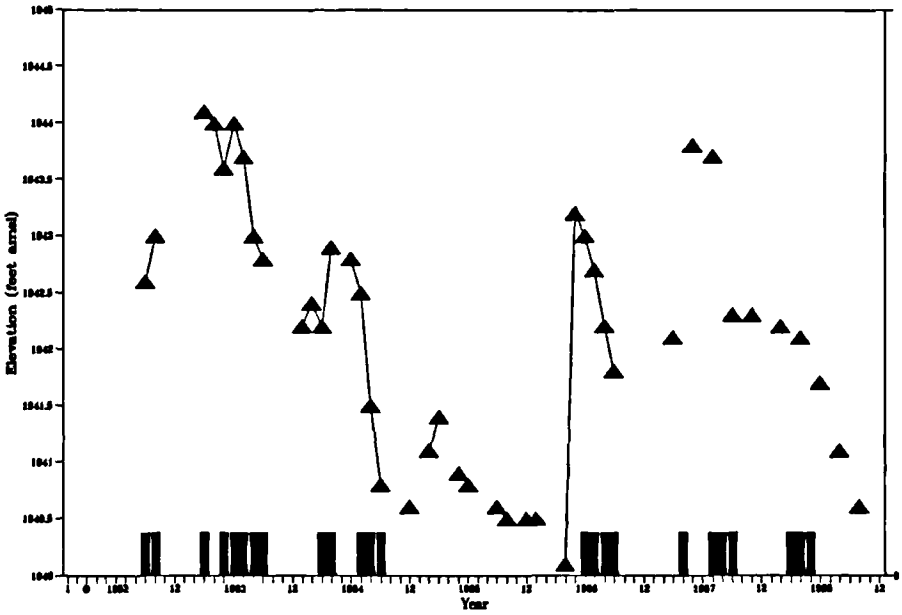
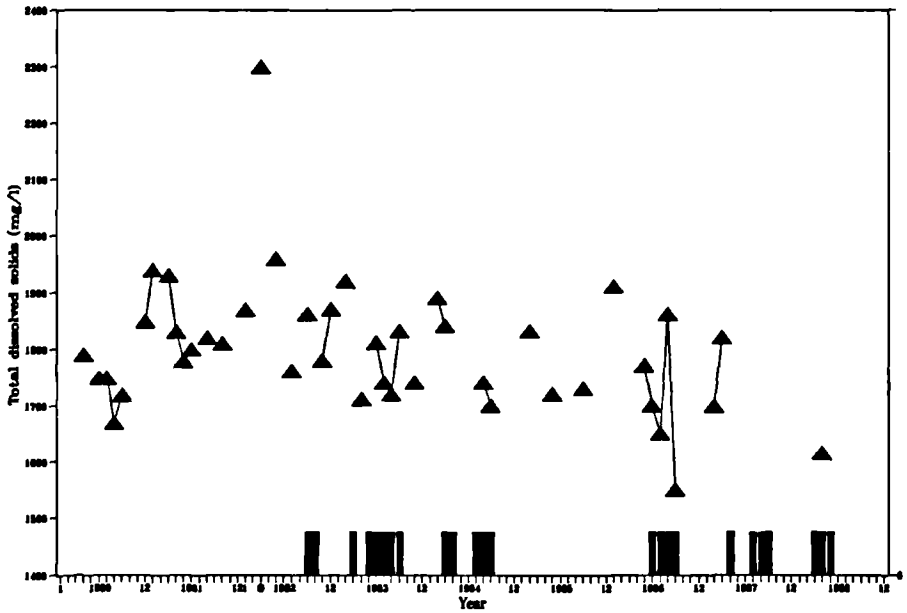


Figure 7.15 - Spiritwood Lake : total dissolved solids (TDS, mg/l) at 0.5m, 1980-1988



Redrawn from data in Sauer (1988)

Figure 7.16 - Spiritwood Lake : total orthophosphate (PO4-P, mg/l) at 0.5m, 1980-1988

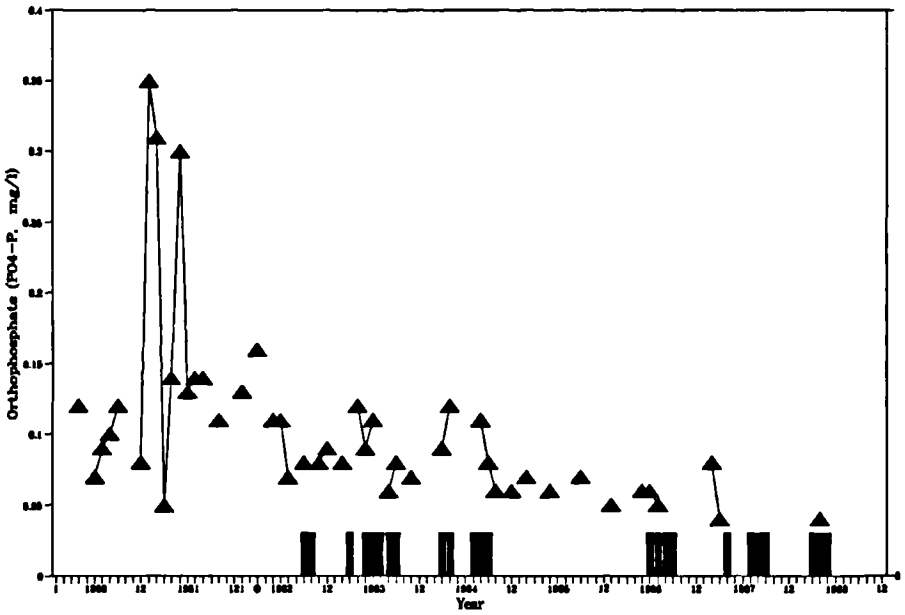
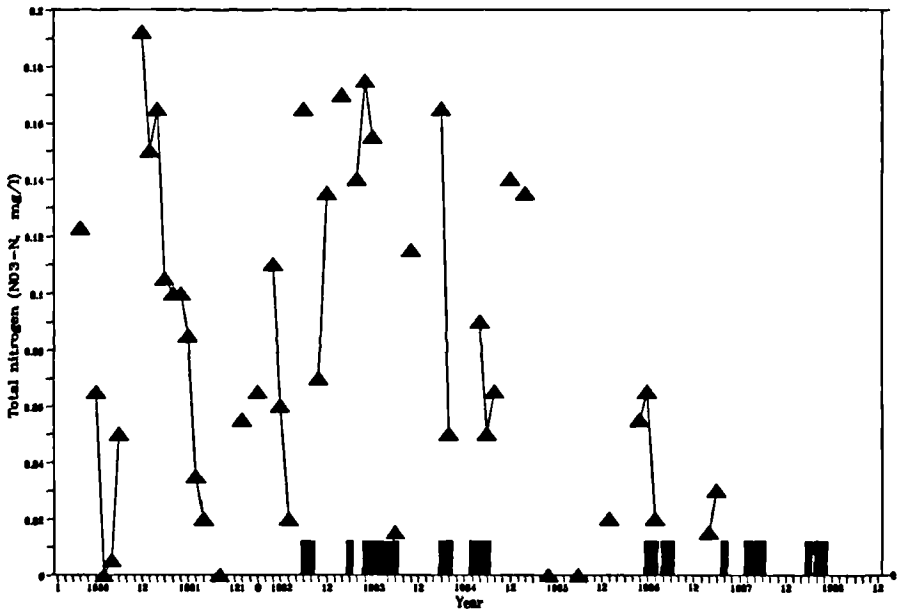
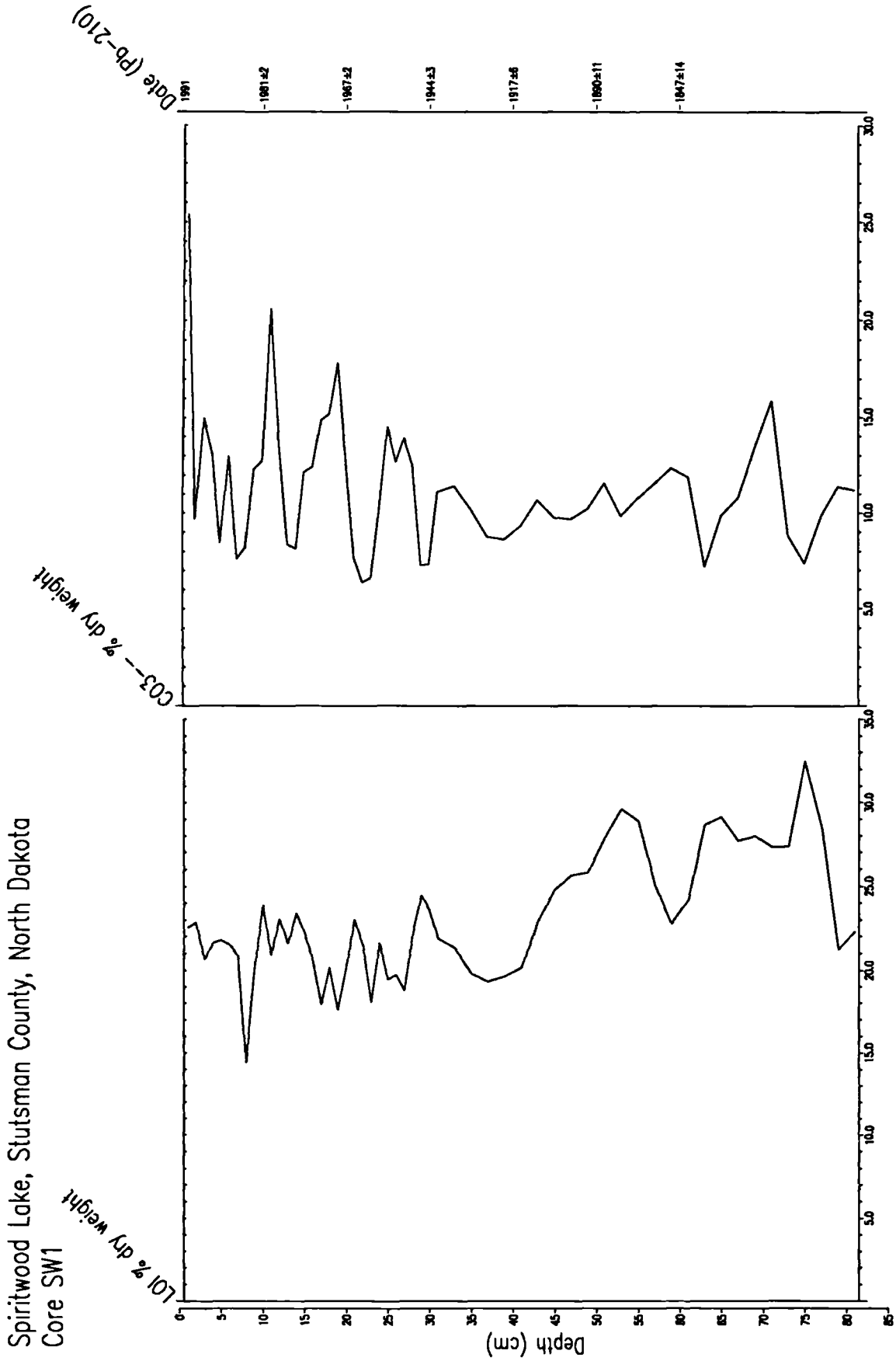


Figure 7.17 - Spiritwood Lake : total nitrogen (NO_3-N, mg/l) at 0.5m, 1980-1988



Redrawn from data in Sauer (1988)

Figure 7.18 Spiritwood Lake core (SW 1): physical analysis



time (see below).

The organic content as a weight proportion is a reflection of in-lake organic productivity as well as dilution by inorganic inputs. The inverse correlation of the carbonate and the organic content broadly points to the closure problem of such data although trends can be highlighted. Carbonate production in high pH and alkaline systems is often authigenic, related to biogenic calcite precipitation (Wetzel & Likens 1983, Stumm 1985). As the catchment is largely calcareous till, major inwash episodes may also be reflected in peaks in the carbonate content record (an allochthonous source). Again, greater variability above 30cms is in part an artefact of sampling, although there appears to be a decadal peak from the early 1960s to 1991, perhaps a measure of periodic inwash events, on top of a slight increasing tendency. Climate may act as a control on catchment sedimentation rates via slope stability (Bickley 1970, Clayton *et al.* 1976). Arid periods promote aeolian erosion and deposition from slopes as vegetation cover is reduced, and subsequent rainfall events can lead to sudden inwash fluxes of material to river (or lake) systems. During the 1930s, 1-2m of sediment was washed into valley bottoms throughout most of the Little Missouri Badlands of western North Dakota (Clayton *et al.* 1976).

7.4.4 Diatom analysis

The diatom record (figure 7.19) covering the period from about 1850 provides evidence for limnological changes, complementary to that of the physical record, from which four palaeosalinity reconstructions were made (figure 7.20, coded as in table 7.6). The flora is characterised by *Stephanodiscus niagarae* and *S. minutulus* throughout much of this period, generally alternating in dominance, while changing frequencies of other taxa point out more subtle changes. Both these taxa are typical of subsaline water (NGP2 WA optima 1.2 & 2.06 g/l respectively), and in common with many *Stephanodiscus* species may indicate eutrophy (Happey-Wood 1988, Anderson 1993, Anderson 1990a, Bennion 1994). The dynamics of species turnover amongst these two taxa are not simply driven by European settlement in the Spiritwood area, as *S. minutulus* and *Cyclostephanos* cf *dubius* are important components before significant permanent settling of eastern North Dakota, both from this diatom sequence, and qualitative examination of samples from an undated 25 m core taken from Spiritwood Lake. These taxa are also found in pre-settlement samples from Devil's Lake (Fritz *et al.* 1991) and Baptiste Lake, Alberta (Hickman *et al.* 1990) during suitable freshwater phases in both lakes' Holocene history.

A slight rise in salinity is indicated in the 1940s-1950s, when *Chaetoceros* cysts (optimum 11.9 g/l, but with a wide tolerance) and *Cyclotella meneghiniana* reach a maximum abundance, and commensurate declines in *Stephanodiscus* taxa. If increases in the relative abundance of the

Figure 7.19 Spiritwood Lake core (SW 1): diatom analysis

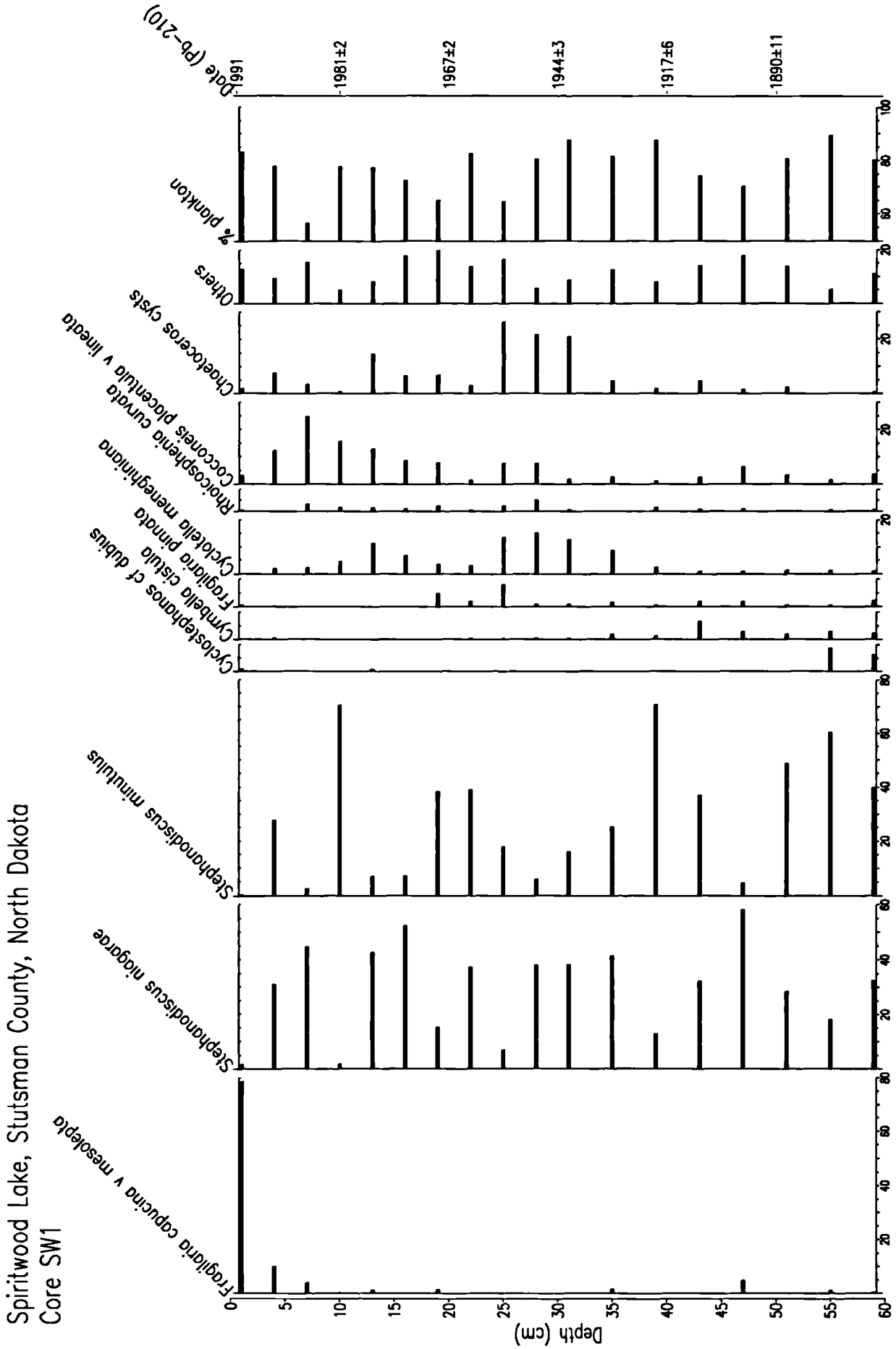
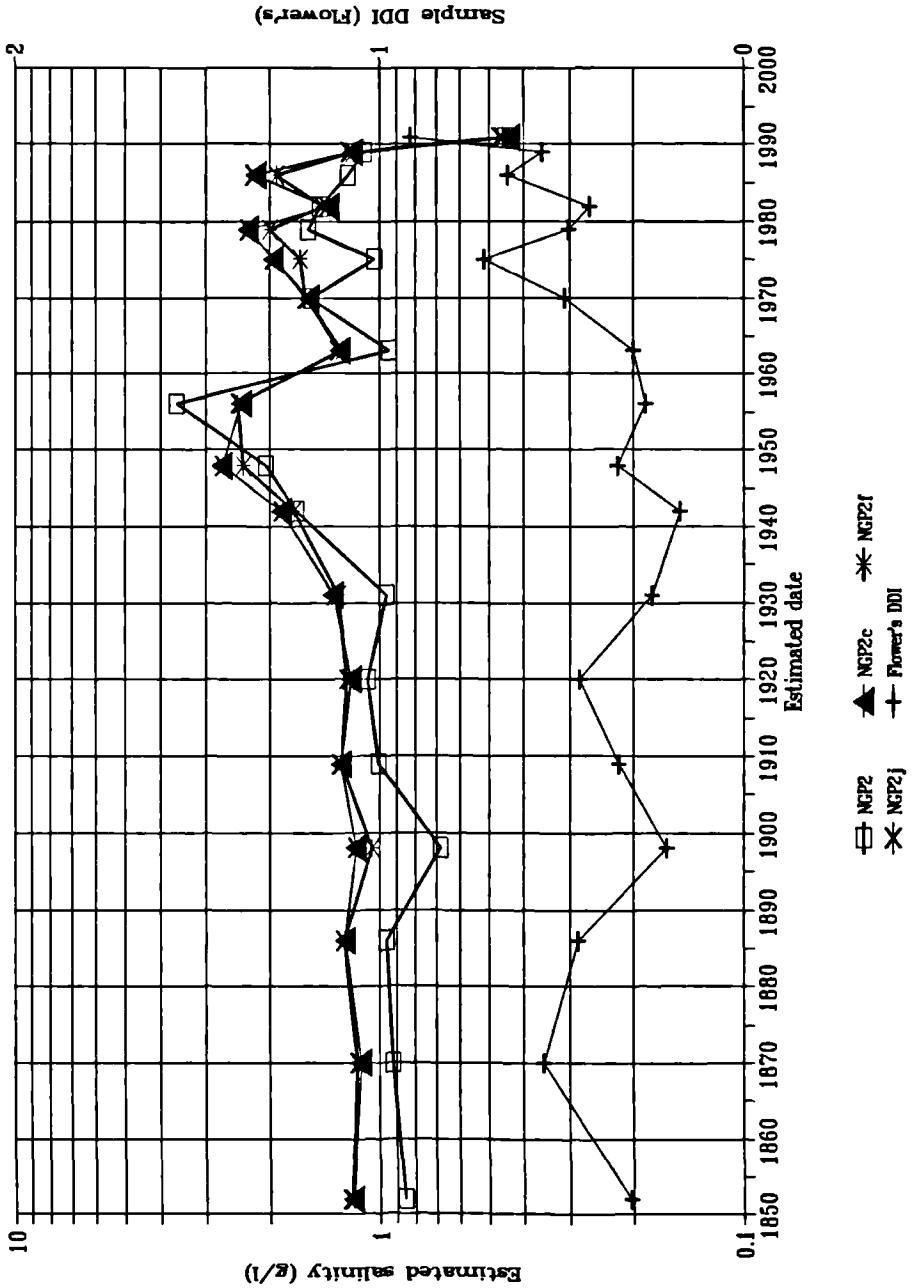


Figure 7.20 : Spiritwood Lake reconstructed salinity & sample dissolution index



epiphytic *Cocconeis placentula* var *lineata* can be interpreted as a lower lake level, and greater areas of macrophyte habitat, rather than less dilution from planktonic taxa, or within-lake transport, this supports salinity trends.

The rise of *Fragilaria capucina* var *mesolepta* at the very top of the core to replace both *Stephanodiscus* taxa appears anomalous compared to the rest of the short core samples and may be the direct result of the lake management scheme. Major changes in the non-diatom phytoplankton community appear to be a direct result of lower nutrient levels, and from the diatom record contained in the short core there have also been major shifts within the diatom flora, despite little change in salinity. The 1991 bloom of *Fragilaria capucina* var *mesolepta* may be an opportunistic response to these sudden but dramatic changes in the lake system, as may the recent decline in both dominant *Stephanodiscus* species.

There is a noticeable drop in both the LOI curve during this time and the planktonic diatom proportion, which may reflect a general decrease in in-lake productivity and absolute diatom plankton abundance, corroborating observations made at the time. The implication is that the usually strong diatom-salinity relationship has also been decoupled to an extent since the late 1980s at Spiritwood, as the salinity reconstructions suggest. Measured salinity since pumping began has fluctuated between 1.5-2 g/l, while the reconstructed salinity of the top sample is largely dependant on the estimated salinity optimum of *Fragilaria capucina* var *mesolepta* (NGP2 optimum 0.027 S-units). The surface sediment sample collected from Spiritwood Lake used in the training set was collected in March 1982, just prior to pumping (the pumphouse was built that summer), and is unaffected by these changes.

It is arguable if such direct manipulation of a lake system can be called restoration in the sense that the pre-settlement state of the lake is not recovered. Limnological conditions (such as nutrient cycling and turnover dynamics) may have been altered, creating a system for which there is no analogue. Complexity is also incorporated via individual competitive efficiency at different ambient levels of macro and micro-nutrients, between the phytoplankton community as a whole, as well as amongst diatoms themselves. Diatoms can successfully compete with other algae if Si:P and Si:N ratios are high (and can be maintained by efficient cycling), and turbidity reduced (Sommer 1988). As cultural eutrophication tends to reduce the first and last of these, diatom abundance may become more seasonal (Sommer 1988). Diatoms commonly comprised only a small proportion of the summer phytoplankton in many prairie lakes sampled. Inherent limnological variability of critical factors such as the timing and extent of lake turnover, temperature regimes and photic conditions in the lake, is introduced on an annual and seasonal basis particularly in lakes such as Spiritwood which are strongly dimictic (Sauer 1988). Responses to salinity are intricately superimposed on these other physiological and ecological

factors.

7.5 Reconstructed salinity at Spiritwood Lake

A record of palaeosalinity derived from the species data under three different weighted models give similar results (figure 7.20), and differ in detail from the control model (NGP2). All models suggest fairly stable, low salinities prior to 1940, which then rise until the 1950s, and fluctuating values from about 1960 to the lowest value recorded in the uppermost sample (1991). Estimated salinity shows more variation under NGP2, and is lower for all samples than any of the weighted versions with the exception of a single sample in the 1950s, which is the only estimate that exceeds the saline threshold value of 3 g/l. Salinity appears to increase consistently from the 1960s until the 1980s under the weighted models to levels almost as high as reconstructed in the 1940s. Too few actual observations of salinity over this period have been found to validate any model with certainty, and the data from the 1980s do not fit any model accurately. Salinity is estimated too low under NGP2, although there is some evidence of a slight freshening towards the end of the decade as the model implies, but the lower value hindcast by all four models in the early 1980s is not corroborated in the available records. The value of about 2 g/l estimated in the mid-1980s for the species weighted models does agree with that quoted in Fritz *et al.* (1993) taken in 1985, although this excursion is not shown in the data of Sauer, which are sparse for that year.

A series of eight measurements of conductivity from October 1976 to September 1978 lend some support to the species weighted models, at least prior to the 1980s. Given the current relationship between conductivity and salinity at Spiritwood, summer salinity was around 2 g/l, which is better represented by models NGP2c & NGP2f. Without a longer record of salinity or conductivity, and no reliable correlation between either of these and lake level, the evidence in support of weighted models as a more accurate means of salinity reconstruction is circumstantial, but where these can be found (as at Devil's Lake) an objective means exists for comparison.

The effect of the Dust Bowl drought period of the 1930s is displaced under all reconstructions, but particularly under model NGP2, which shows a skewed response peaking in the 1950s and sudden freshening (by comparison) in the 1960s. The increase in salinity under the weighted models is less extreme, and peaks during the late 1940s, slowly freshening over the next 15 years. Devils Lake shows a similar delayed response (Fritz 1990), reaching its lowest lake level in 1940 (*Stutsman County Record*, June 22nd, 1950) and not freshening appreciably until 1950, although lake levels there had been in decline since at least the turn of the century.

7.6 Salinity and diatom dissolution at Spiritwood Lake

Figure 7.20 shows the variation in Flower's DDI (excluding *Chaetoceros* cysts) for the Spiritwood samples, over time, and the relationship with salinity. Values are similar to those reported from sedimentary diatom assemblages from Lake Baikal (Flower & Likhoshway 1993). There is no apparent trend with time, nor is there evidence of a systematic variation with salinity, although the lowest level of dissolution is found in the uppermost sample, coincident with the lowest inferred salinity (at the subsaline threshold of 0.5g/l). Sample dissolution index appears to follow salinity as reconstructed by model NGP2 before 1950, and inversely after 1970, but less evidently with weighted models. Figure 7.21 demonstrates that even with all three dissolution indices (Flower's, weighted average and square weighted average; Chapter 5) there is little consistent trend with salinity (model NGP2c), or time, whether adjusted or not for *Chaetoceros* cysts, which cannot be reliably classed in stages (Chapter 5).

The relationship between Flower's dissolution index for the two main taxa, *Stephanodiscus niagarae* and *S. minutulus* shows some consistency (figure 7.22), with broadly similar degrees of dissolution for many samples. Exceptions are samples dated 1989, with relatively well preserved *S. niagarae*, and 1920 and 1948, in which *S. minutulus* is well preserved. Unequal dissolution may indicate reworking, of *S. minutulus* in 1989 and *S. niagarae* in 1920 and 1948. If further studies can show that these anomalies are real and simultaneous lake-wide phenomena, rather than sedimentation processes at the micro-scale, competing hypotheses (Chamberlain 1898) can be generated that sedimentation and core studies, and comparison to instrumental records, for example, can test. Marginal lake sediments may be reworked if lake level falls (a possible explanation for 1948), or unusual storm events may be responsible, assuming that the dissolution behaviour of taxa is approximately the same over this time scale.

Generally better preservation of the less robust *S. minutulus* (according to experiment) may itself appear anomalous, but the ranking method is based on the robustness of taxon-identifying parts attributable to one individual valve, and in itself says nothing about the condition of the valve. Perhaps more importantly, controlled laboratory dissolution is only a simplified approximation to one taphonomic process operating in lakes, and although the results are encouraging, further research on *in situ* lake dissolution is needed.

7.7 The record of climate change at Spiritwood Lake

7.7.1 Historical records of climate

Meteorologic data for Jamestown Hospital, 16 miles south-west of Spiritwood Lake from the

Figure 7.21 Spiritwood Lake core (SW 1): dissolution indices

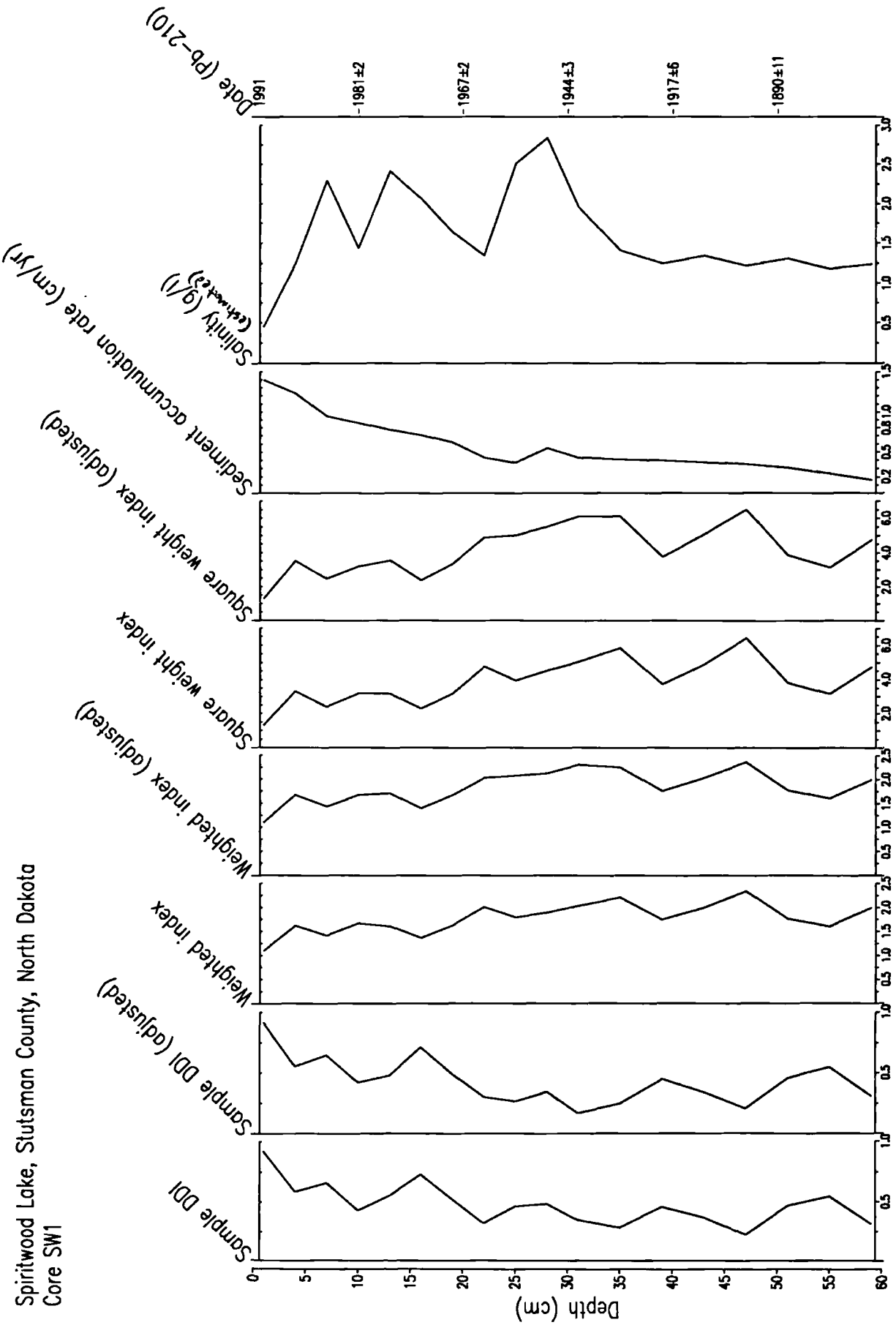


Figure 7.22 : Flower's DDI for *Stephanodiscus niagarae* against *S. minutulus* (Core SW1)

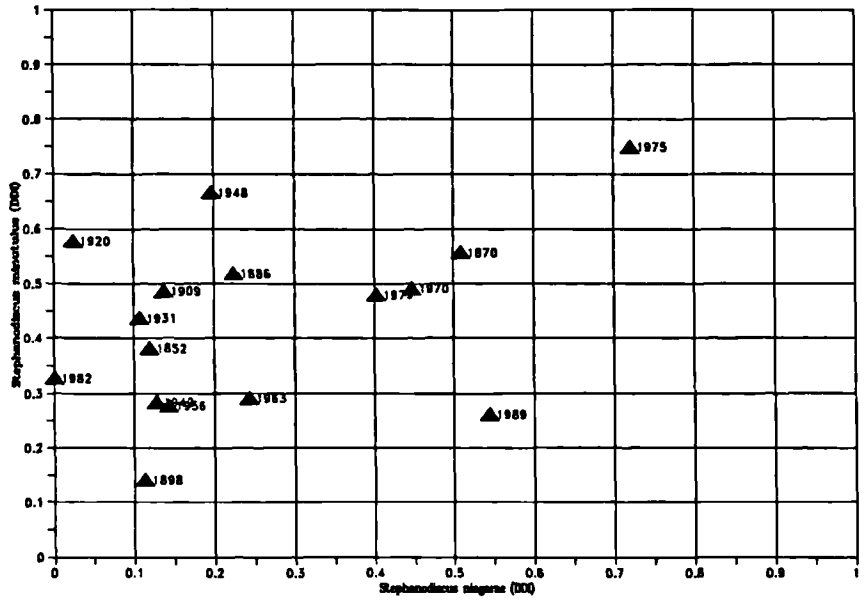
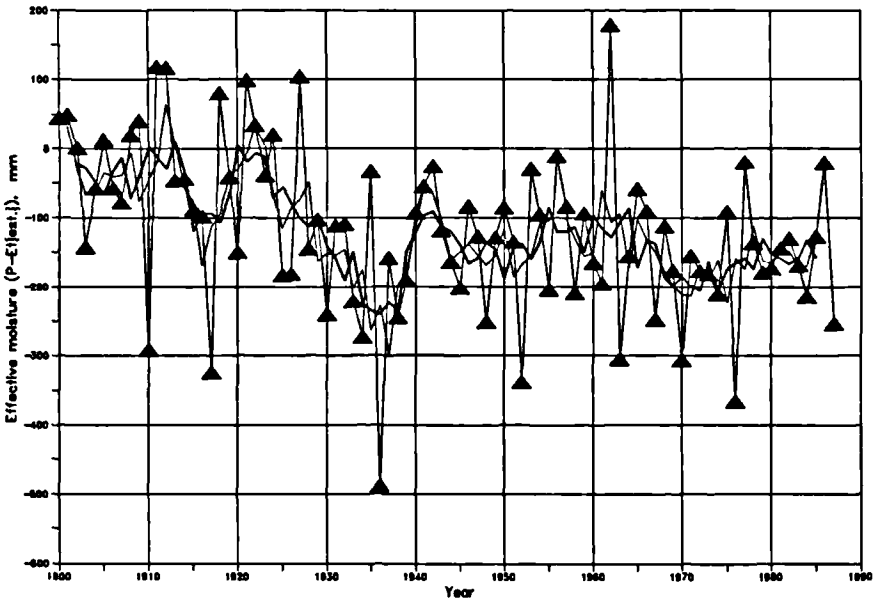


Figure 7.23 : Estimated moisture balance, Jamestown, North Dakota, 1900-1987



Oak Ridge National Laboratory Historical Climatology Network was furnished by Dr. Diane Larson, North Prairie Wildlife Research Center, Jamestown. Records of mean monthly temperature and precipitation from 1900-1987 were transformed into annual moisture balance estimates, based on the methods of Thornthwaite (1948, in Wilson 1986, Ward & Robinson 1990). Potential evapotranspiration figures derived from temperature are prone to underestimate actual annual figures in arid and semi-arid regions (Ward & Robinson 1990) but highlight climatic trends on a broader timescale. Annual moisture balance for Jamestown are presented in figure 7.23, which also gives 3 and 5 year averages. For comparison, current deficits in the region are estimated at around -300mm/year (in Fritz *et al.* 1993).

The 1930s were a period of enormous economic and social hardship for much of the United States, but depression was exacerbated in the mid-West by a combination of drought and farming practice, particularly wheat monoculture (Drache 1970). The early years of statehood (1889) coincided with generally high precipitation, which together with the cheap or free land claims attracted predominantly farm settlers, particularly eastern European and Scandinavian immigrants. It has been estimated that the population rose from 154,074 in 1890 to 577,056 in 1910, by which time 14,502,642 acres were under cultivation (Baker 1976).

During the 1930s, it is estimated that one-third of the North Dakota's population lived on relief at any one time, while hundreds of farms were abandoned. Dust storms were frequent and severe enough to alter local topography (Kress & Pfaller 1967, Clayton *et al.* 1976), earning the label of the "Dirty Thirties". Although the worst year climatically was 1934, and the most extreme 1936 (including the longest consecutive period of both coldest and hottest temperatures ever recorded in North Dakota, and the least precipitation; Kress & Pfaller 1967), widespread drought continued until 1940.

7.7.2 The sensitivity of Spiritwood Lake to climate change

Periodic drought has been a feature of the Northern Great Plains for much of the last 8,000 years of the Holocene, the more sensitive sites with highest resolution records (such as Devils Lake) demonstrating the extent and rapidity of change. Devils Lake has undergone several cycles from about 1-40 g/l TDS (Fritz *et al.* 1991) over this period, the most saline around 8,000 yBP, at which time aridity appears to have been widespread over the region (Cvancara *et al.* 1971, Webb *et al.* 1983). Climatic conditions may compare to those of 1930-1940, during which decade, mean annual temperature was 2°-3°C higher than usual, and precipitation about 100 mm less than usual (Clayton *et al.* 1976).

Palynological evidence from a 14m core taken from Spiritwood Lake, points to significant

vegetational change over the Holocene (Dr. J.H.McAndrews, unpublished data) at the lake itself, although diatom evidence from a second 25m core suggests the lake water has remained fresh. Spiritwood Lake, although affording a high resolution record of environmental change, is conspicuously insensitive to minor fluctuations in regional climate.

The deterioration of climate culminating in the Dust Bowl years of the 1930s can be traced back to the early part of this century (figure 7.23). Early records of drought and isolated lake level changes exist for Spiritwood but most go unrecorded in the salinity reconstruction (figure 7.20). Droughts are known in the region in the early 1860s, 1886, 1899-1900, 1909-1910, 1919, 1930-1940, and 1963-1964 (Ramirez 1975, Baker 1976, Brother Philip Kress, pers. comm.) and lake level fluctuations of several feet at Spiritwood have been known historically.

Lake level rose "considerably" in 1895 (*Jamestown Daily Alert*, May 26, 1896), and in 1900 fell over 8 feet in a year (Johnson 1950). A bathymetric survey, referred to in Johnson (1950) carried out by a Northern Pacific Railroad geologist, in 1889, found the greatest depth was 44 feet (currently 53 feet), which shore-line evidence suggested was lower than usual, and was known to have been higher in 1880 and 1882. The same plumb-line method has measured depths of 58 feet (Johnson 1950) at unspecified times since. Such changes are significant in terms of lake volume, as from hypsographic calculations from figure 2.3, with current lake bathymetry and level, a fall of 5 feet corresponds to a reduction in volume of 9.4%, while a drop of 10 feet implies a reduction in volume by 30%. Spiritwood Lake level may show considerable fluctuation with annual moisture balance but salinity only appears to respond to a more prolonged and extreme climatic shift, exemplified by the 1930s.

7.7.3 The role of groundwater at Spiritwood Lake

Anecdotal evidence supports the contention that Spiritwood Lake has long been a freshwater lake. Sioux Indian folklore, often an invaluable and highly accurate source of pre-European history, has always known Spiritwood Lake as Mini-eskaya (McBeede in Johnson 1950). This phrase, literally translated, means "water with white foam", and was applied to freshwaters, including rivers, which were sources of drinking water, an important commodity in the Plains Indian culture. Other reference is made to the importance of subsurface flow at Spiritwood. The natural surface outlet of Spiritwood Lake, the Big Coulee to the south-west, regularly flowed in the 1880s but even when dry, water was found to flow several feet below the surface. Groundwater flows were cited as the reason that an area in the centre of the lake does not freeze over in winter (Johnson 1950).

The permanence and depth of the lake points to a possible explanation in the groundwater

flows that must dominate the lake water budget in an region of annual moisture deficit. The role of groundwater in determining lake salinity is poorly understood, although it is recognised that flow pathways, and relative position within the watershed can create major differences in lake chemistry within over small distances (Almendinger 1990) and short time periods (Arndt & Richardson 1993), a feature of prairie lakes. Subsurface flows acting as a source and sink of water and salts at Spiritwood, might function as a buffer to regional changes in moisture balance.

The evidence suggests that Spiritwood Lake salinity is only responsive to extreme and prolonged climatic shifts. The implication from this is that the salinity rise after the 1930s drought period was the response once a threshold of water deficit perhaps over several decades was reached. Such damped and delayed responses to an ostensibly closed lake can only be explained by a system that is dominated by lagged groundwater flows and geochemistry.

Chapter 8
Conclusions

8.1 The nature of saline lakes

Saline lakes are complex and highly variable systems, about which relatively little is known, from an ecological or physico-chemical viewpoint. These environments are of considerable importance, from an economic, ecological and increasingly palaeoecological perspective, which has only recently begun to be exploited.

This variability must be taken into consideration when sampling strategies for ecological and palaeoecological research are designed. In particular, seasonal and secular changes in salinity, and ionic composition, may cause a mismatch between sediment assemblages and environmental parameters measured at the time of collection.

Sample unrepresentativity is also a product of taphonomic processes in saline lakes, which include processes not found often in freshwaters, such as meromixis, lake desiccation and intrasedimentary crystal growth, as well as common problems of sediment mixing, focusing and source community representation. Sampling strategies should aim to take such features into account, both spatially (multiple sampling throughout the lake basin, *e.g.* Bradbury & Winter 1976, Anderson 1989, Allott 1991) and temporally, visiting sites throughout the year to monitor seasonal cycles and other changes.

8.2 Sample preparation

Previous research (*e.g.* Flower 1993, Boden 1991) has implicated the role of sample storage and processing in altering microfossil assemblages, in addition to those acting within the lake. The present study has affirmed that even standard and supposedly "gentle" techniques can, in certain circumstances, lead to significant sample losses and assemblage bias. Care must be taken to ensure field and laboratory processes are suitable for the aims of the research.

8.3 Experimental methodology

An experimental procedure was developed for controlled dissolution of fresh and recently sedimented diatom frustules at room temperature and pH10 over several weeks. Several different assemblages could be linked by the behaviour of taxa common to each. The progress of dissolution was followed by changes in valve abundance, dissolved silica concentrations, and

species composition. Parallel to this, morphological changes in the valves were monitored under scanning and light microscopy. Dissolution in salt solutions was not an appropriate experimental approach, and although many feasible experimental dissolution methods exist, which is best in any situation depends on the experimental and research aims.

8.4 Dissolution stages and indices

Dissolution experiments provide a basis for ranking taxa by susceptibility to dissolution according to changing species composition, for which several methods exist. These generally give similar results, within the confines of counting procedure and accuracy.

Generally, taxa which appear weakly silicified under the light and electron microscope are more susceptible to dissolution, such as *Nitzschia* species, and *vice versa*, although gross valve morphology is not always an accurate guide. Consistent differences in rank are found between the raphid (less robust) and rapheless valves of *Cocconeis* species, which may reflect the role of valve breakage as dissolution proceeds. "Robustness" derived from counts of species percentages, is also a function of the point at which valve fragments cannot be identified, which biases those with distinct terminal stages (such as many *Navicula*, *Mastogloia* and *Cyclotella* species). Such taxa can be used to characterise the dissolution status of an assemblage.

Morphological changes could often be categorised into distinct and recognisable dissolution stages for a wide range of taxa. This permits the development of indices based on the changing proportions of valves in each category. Different indices can be used to highlight separate aspects of the data, such as Flower's DDI, and weighted average indices, and their complementary use is encouraged. Dissolution indices can be related to total abundance changes within experimental assemblages.

8.5 Multivariate statistical techniques

Ecologically-derived multivariate methods can be applied in two distinct ways with data from dissolution experiments. Predictive models of dissolution parameters can be developed from empirical observations for assemblages. These methods can be used for estimating silica loss, for example, from natural assemblages (Pichon *et al.* 1992), but must be calibrated by dissolution experiment.

Separately, dissolution ranking can be applied to weighted averaging transfer functions (Birks *et al.* 1990) for reconstructing ecological parameters, as a proxy for sample preservation. A salinity transfer function developed from a 55 lake database from the Northern Great Plains

underestimates high salinities when compared to an historical record of salinity at Devils Lake, North Dakota (Fritz 1990). Variable weighting of samples, species or both often slightly improves the model in terms of r and RMSE, where species ranks are known from experiment and not estimated on morphological similarity to ranked taxa.

Weighting species abundance is shown to give different reconstructed salinity down a short core from Spiritwood Lake, but no independent means exists from observed salinity or lake levels at this site to determine the accuracy of any model. Actual model improvements can only be assessed by validation at sites with a known salinity history, such as at Devils Lake.

Saline lakes in the Northern Great Plains have different sensitivities to environmental and climatic change, and if calibrated against observed records, a means exists of evaluating the relative magnitudes, timing and spatial extent of these events over the Holocene. Spiritwood Lake salinity only records extreme climatic signals, and exhibits a lagged response.

8.6 Future research

8.6.1 Experimental

Dissolution experiments on other diatom taxa can be linked to the present ranking system by including taxa whose dissolution behaviour is known. Further experimental work can explore the relationship between species dissolution index and abundance decline, in a predictive manner. For some taxa, it may be possible to estimate what proportion of valves have been lost from the death assemblage. It is only possible to reconstitute the death assemblage from what is present in a taphonomically altered sample, as nothing can be said about populations of which nothing remains. Although dissolution experiments can aid an understanding of taphonomic processes in saline lakes, degradation destroys information which is irrevocably lost.

8.6.2 Palaeolimnological

Results indicate that the NGP salinity transfer function could be improved in accuracy if sample preservation can be treated within the transfer function. Diatom analysis with dissolution stage subdivisions can be used to screen samples in the NGP training set, and may provide another means of weighting according to preservation state, perhaps complementary to species weighting according to experimentally-derived dissolution ranks. Devils Lake may be a useful trial of such an approach, as it has an independent record of salinity.

8.7 Summary

The last 150 years in this region of the Northern Great Plains have been witness to massive changes in the landscape that have transformed the native prairie grassland to an essentially cultivated and managed cereal culture. Natural environmental change has been superimposed on and synergistic with that of European settlement, to the extent that it is not always possible to disentangle the two in contemporary systems. Palaeolimnological techniques are a means of establishing such baseline conditions, using biological and physico-chemical data as environmental proxies.

Environmental reconstructions based on proxy data are only as sound as the assumptions necessarily made to simplify a problem of multivariate complexity. Saline lake systems are complex and to some extent unpredictable, but nonetheless rich, sinks of environmental information. Diatom transfer functions have been shown to predict and reconstruct salinity with high accuracy, and results suggest that approaches incorporating the differential susceptibility of taxa, and unequal preservation states of sediment samples, can improve their utility as tools of palaeolimnological research.

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Dissolution stages for some major morphological groups

Stage 1 is the pristine condition in all cases.

Amphora

Stage 2 Striae at distal raphe ends dissolve & coalesce. Areolae enlarged throughout valve.
Stage 3 Valve dissolves from distal raphe ends, particularly along dorsal margin, which may quickly disappear.
Stage 4 Central hyaline area of thicker silica remains; raphe, if present, vestigial. No striae remain.

Anomoeonis

Stage 2 Areolae/ocelli enlarged; valve walls noticeably thinner
Stage 3 Valve dissolves from margins to raphe, and from apices to centre. Valve may split along raphe canal. Identification is by central area.

Campylodiscus

Stage 2 Inter costal area corrodes at margin; central area persists.
Stage 3 Central area tends to dissolve before the marginal ribs, which are progressively exposed. Raphe and ribs remain, usually at expense of intercostal and central areas.

Cocconeis - (araphid valve)

Stage 2 Areolae enlarged; marginal rim dissolved. Valve may split along apical axis.

Cocconeis + (raphid valve)

Stage 2 Areolae enlarged; raphe often resists dissolution relative to the surrounding valve face. Valve may split along raphe.

Cyclotella

Stage 2 Intercostal areas dissolve but marginal rim remains.
Stage 3 Costae remain but marginal rim dissolved.
Stage 4 Costae dissolved or vestigial; central area (with processes enlarged) may survive as a featureless disc.

Cymbella

Stage 2 Distal valve ends dissolve from both margins towards raphe.
Stage 3 Raphe and central area remain; striae dissolved but silica ribs separating striae remain. Both margins dissolved.

Naviculoid pennate - e.g. Navicula oblonga, Mastogloia spp.

Stage 2 Chambers of striae coalesce, especially at distal raphe ends. Valve outline maintained. Margins remain.
Stage 3 Valve dissolves from distal apices towards central area. Valve margins distinguishable towards centre.
Stage 4 Central area only remains, with vestigial raphe canal.

Nitzschia

Stage 2 Areolae coalesce; striae dissolve; often raphe (and keel punctae) only remain.

Stephanodiscus

Stage 2 Areolae enlarged and may coalesce; margins remain. Spines often corroded, irregularly preserved.
Stage 3 Valve dissolves from margin towards central area; margin dissolved. Spines disappear.

Surirella

Stage 2 Inter costal area corrodes at margin; central area and raphe persists.
Stage 3 Marginal raphe and central area remain; intercostal area dissolved.

Synedra

Stage 2 Striae chambers coalesce and dissolve at valve margins; valve apices distinct.
Stage 3 Valve dissolves towards central area from apices.

Appendix 1 - Figure A1.1

Amphora coffeaeformis

a Dissolution stage 1 (LM). Scale bar = 9 μm

b Dissolution stage 1 (LM). Scale bar = 8 μm

c Dissolution stage 1 (SEM)

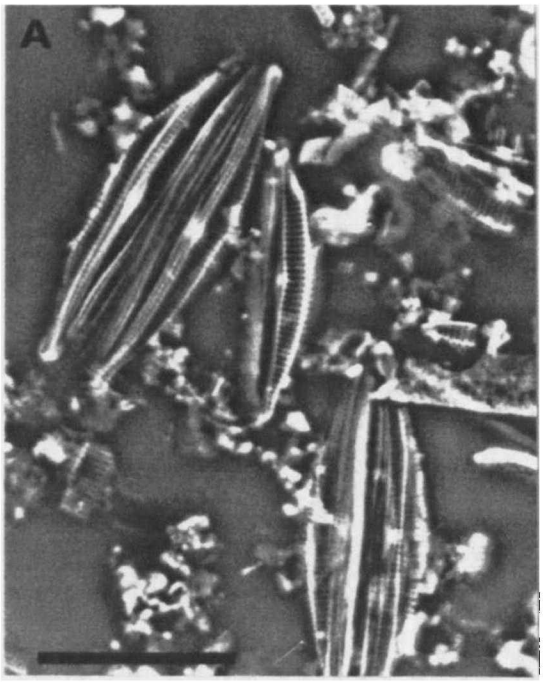
d Dissolution stage 1 (SEM)

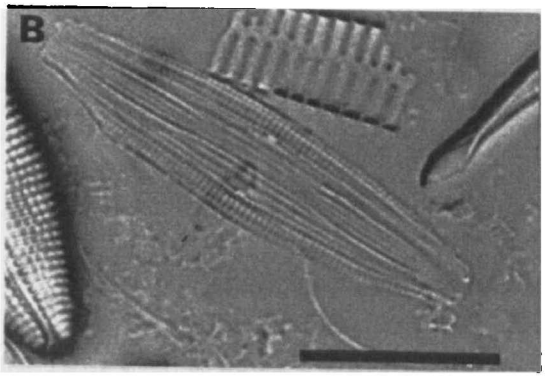
e Dissolution stage 1 (SEM)

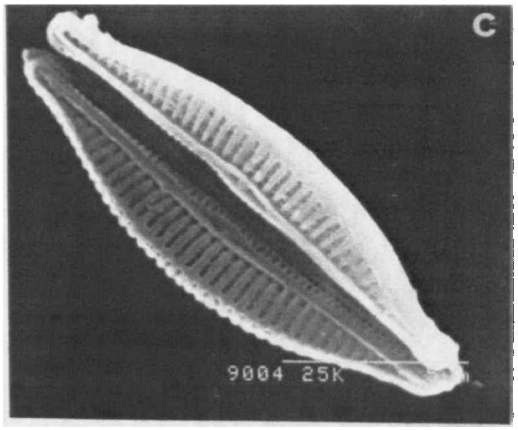
f Dissolution stage 1 (SEM)

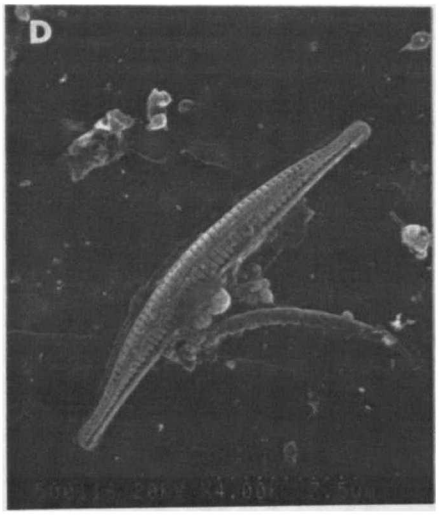
g Dissolution stage 2 (SEM)

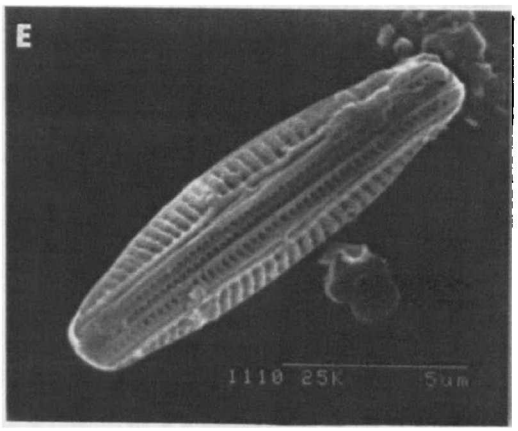
A1.1 a – g

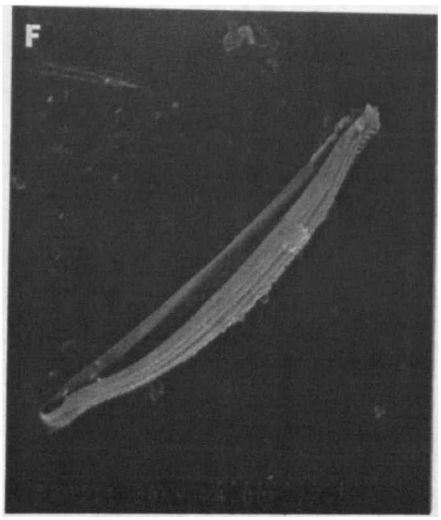


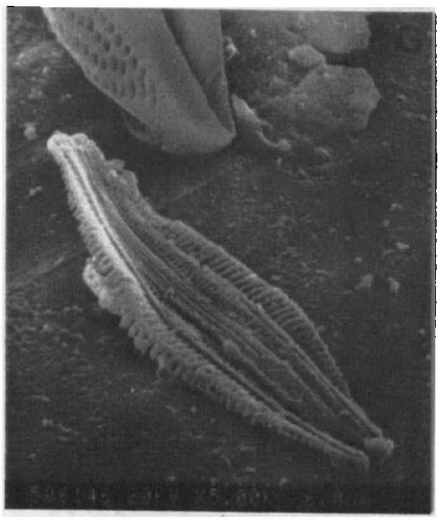












Appendix 1 - Figure A1.2

Amphora libyca (a-f) and *A. pediculus* (g)

a Dissolution stage 1 (LM) - focus A. Scale bar = 18 µm

b Dissolution stage 1 (LM) - focus B. Scale bar = 18 µm

c Dissolution stage 1 (SEM)

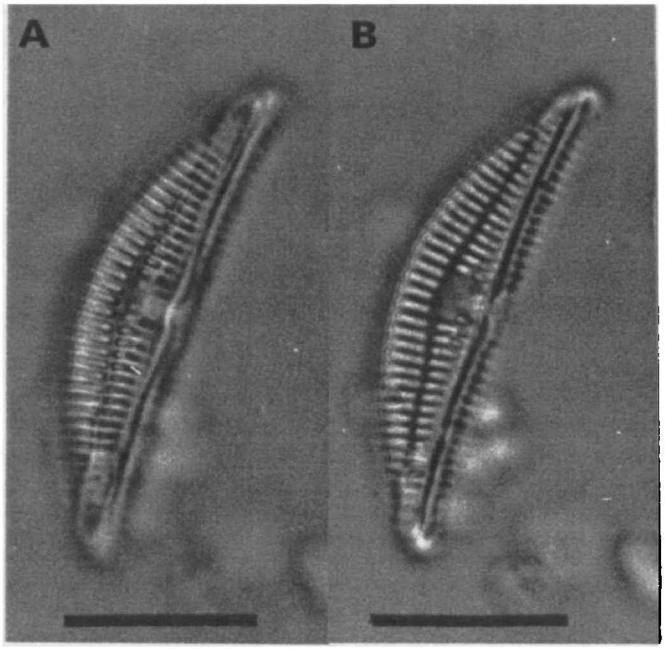
d Dissolution stage 2 (SEM)

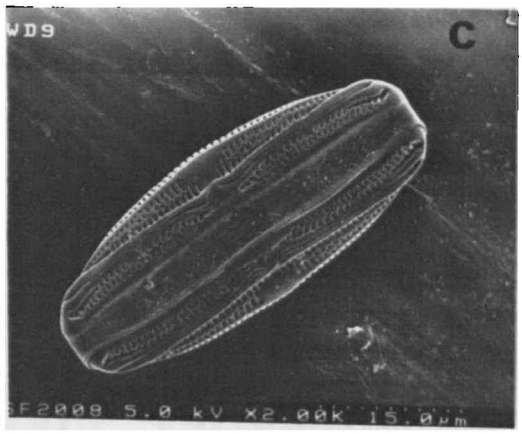
e Dissolution stage 2 (SEM) - detail of **c**

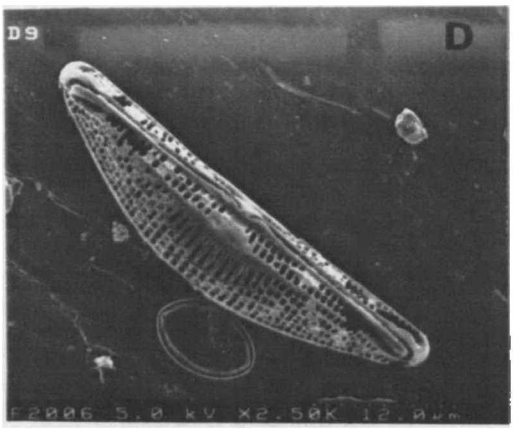
f Dissolution stage 2 (LM). Scale bar = 16 µm

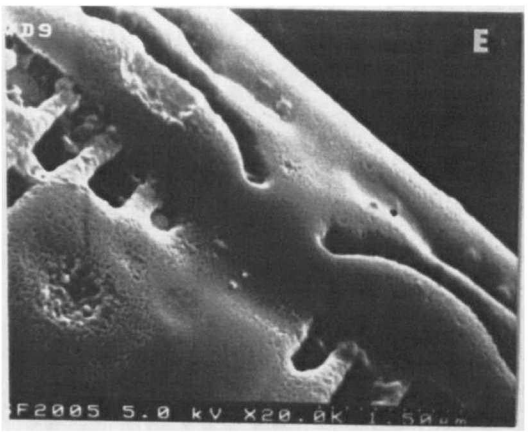
g Dissolution stage 1 (SEM). Note spongy texture to frustule.

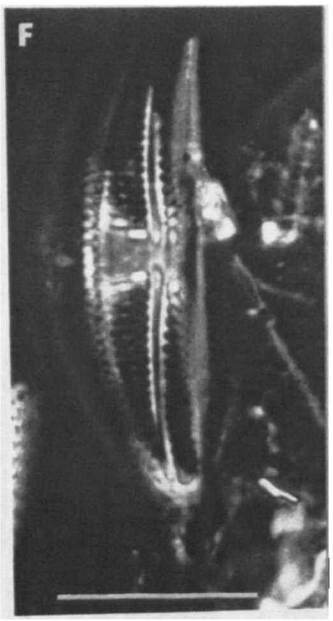
A1.2 a–g

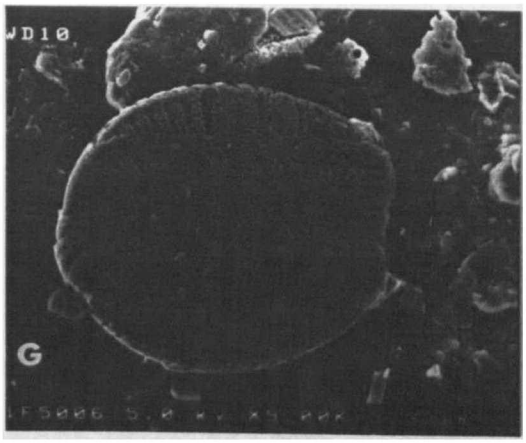












Appendix 1 - Figure A1.3

Amphora libyca **(a & b) and** ***Brachysira aponina*** **(c-f)**

a Dissolution stage 3 (SEM)

b Dissolution stage 4 (SEM)

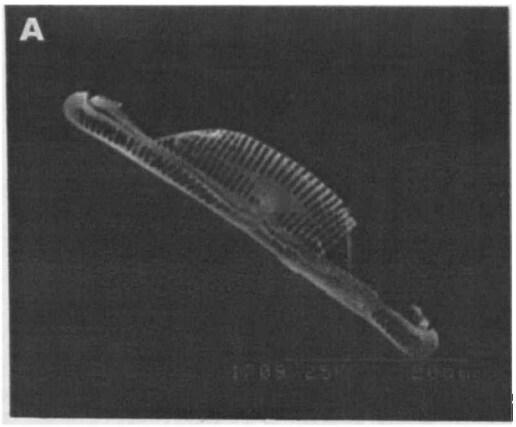
c Dissolution stage 1 (SEM)

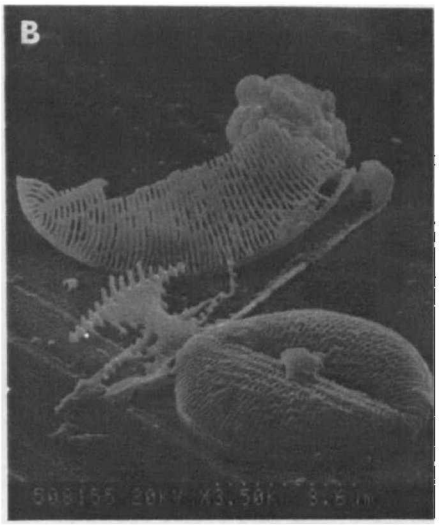
d Dissolution stage 1 (SEM)

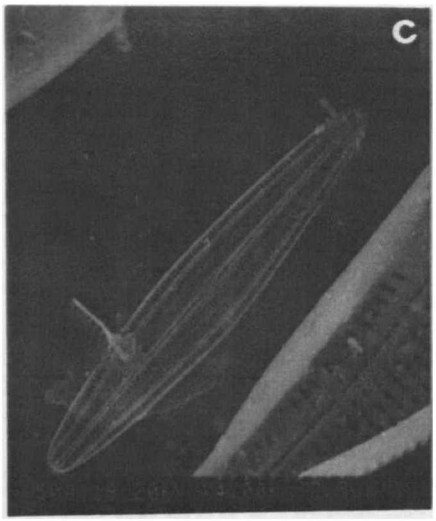
e Dissolution stage 1 (SEM)

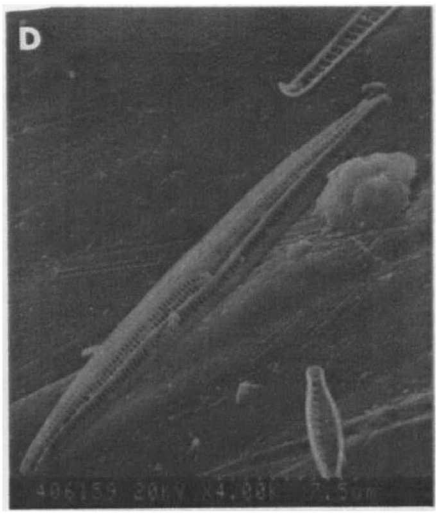
f Dissolution stage 2 (SEM)

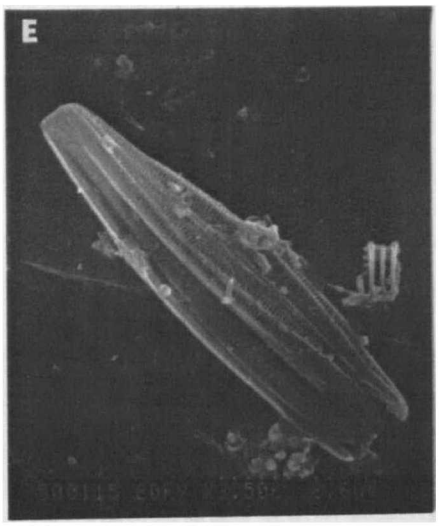
A1.3a–f

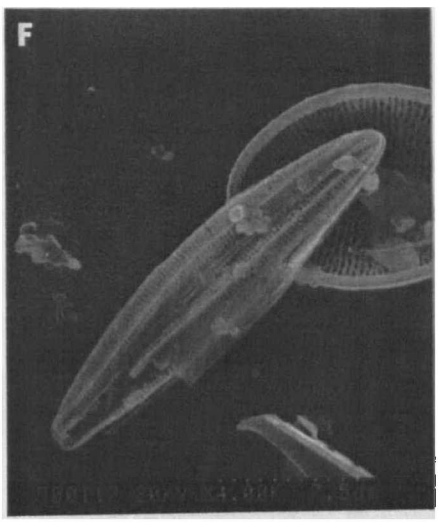












Appendix 1 - Figure A1.4

Anomoeoneis costata

a Dissolution stage 1 (LM) - focus A. Scale bar = 15 µm

b Dissolution stage 1 (LM) - focus B. Scale bar = 15 µm

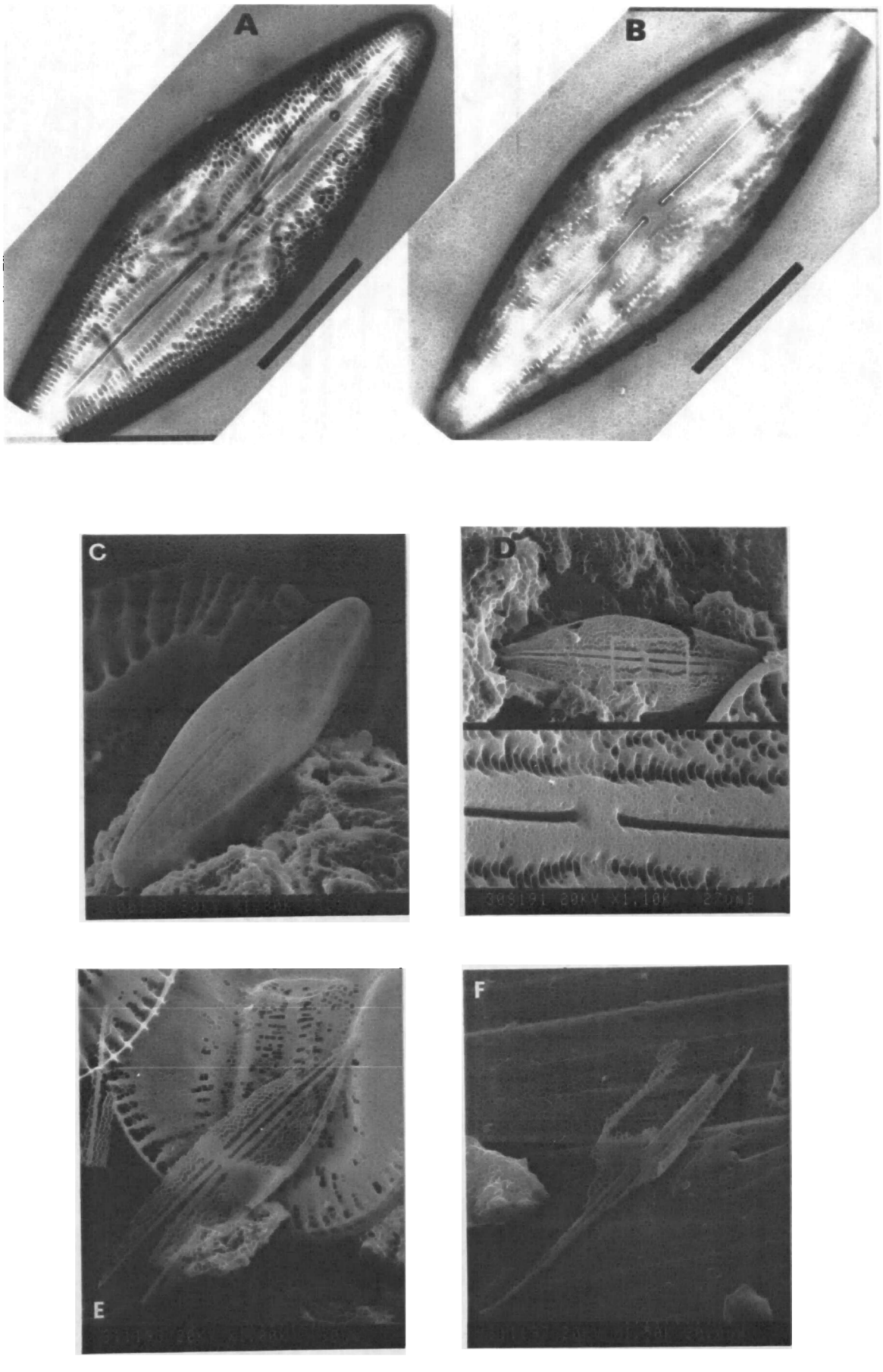
c Dissolution stage 1 (SEM)

d Dissolution stage 2 (SEM). Detail shows dissolution around raphe and punctae enlargement

e Dissolution stage 3 (SEM). The valve may split along the raphe, which is usually the most robust structure (see **f**)

f Dissolution stage 3 (SEM). The valve remains identifiable by the central area and thickly silicified raphe canal

A1.4a–f



Appendix 1 - Figure A1.5

Campylodiscus clypeus

a Dissolution stage 1 (LM). Scale bar = 45 µm

b Dissolution stage 1 (LM). Scale bar = 40 µm

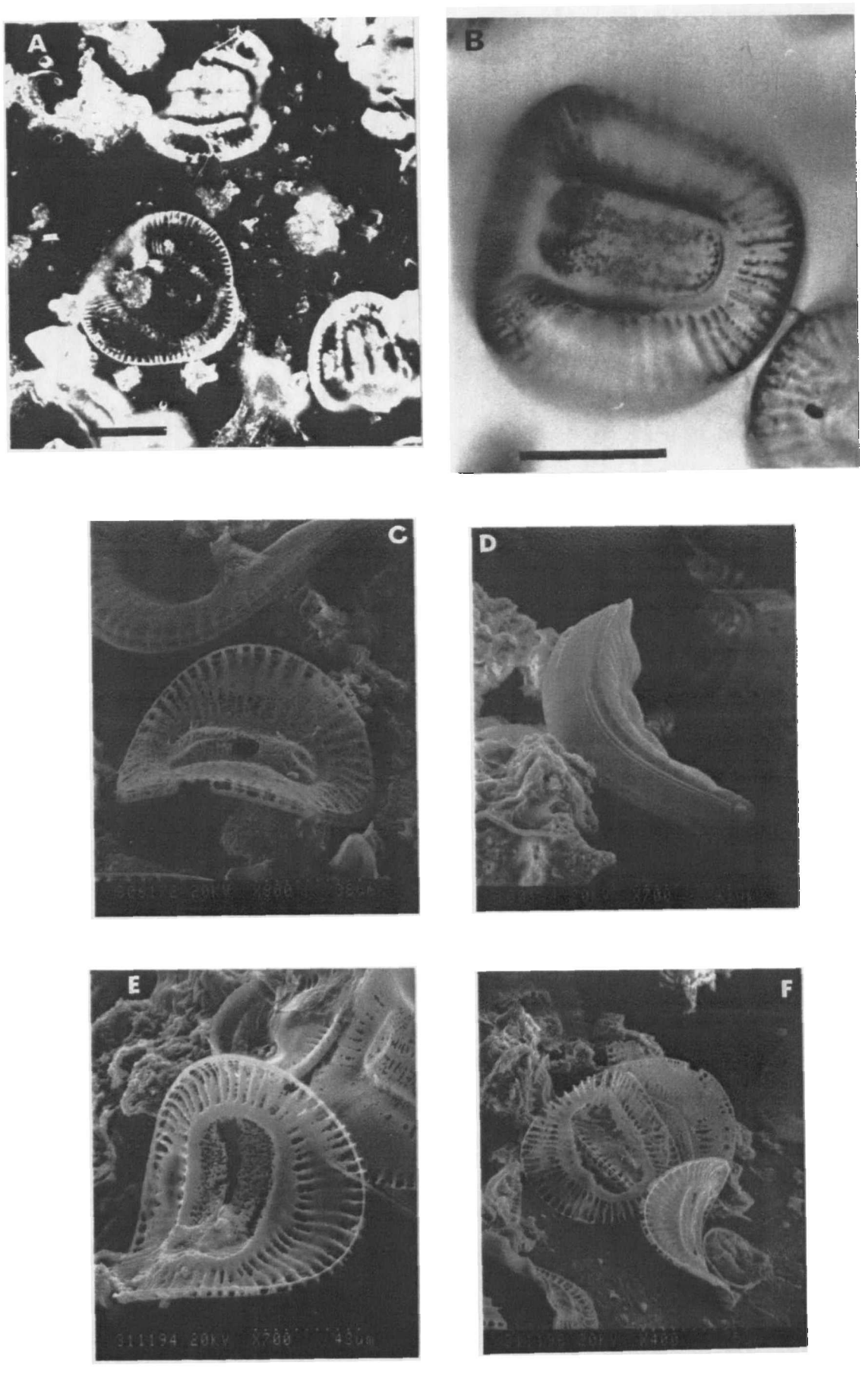
c Dissolution stage 2 (SEM). Note corrosion of the inter costal area at the margin.

d Dissolution stage 1 (SEM), girdle view.

e Dissolution stage 3 (SEM). The central area tends to dissolve before the thicker marginal ribs, which can be clearly seen at this stage.

f Dissolution stage 3 (SEM). The relative weakness of the central area is exploited by preferential dissolution (and breakage). Identification is by the remaining marginal ring and ribs, as the central area is usually not found whole (see **c** and **e**).

A1.5 a – f



Appendix 1 - Figure A1.6

Chaetoceros cysts

a Fresh planktonic bloom from Coldwater Lake, live sample as collected (with a minor component of *Cyclotella quillensis*). Scale bar = 40 µm (LM)

b Fresh cells, with thin silica wall surrounding robust cyst capsule (LM). Scale bar = 6 µm

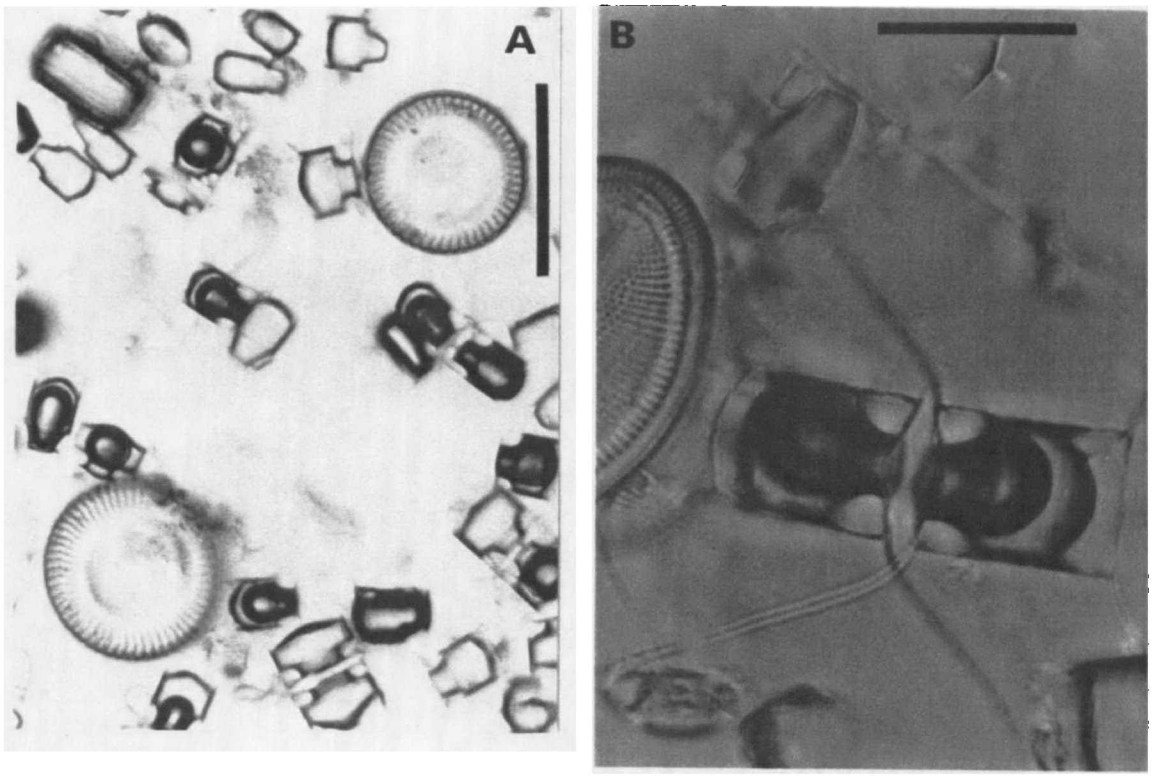
c Resistant cyst, essentially featureless and heavily silicified (SEM)

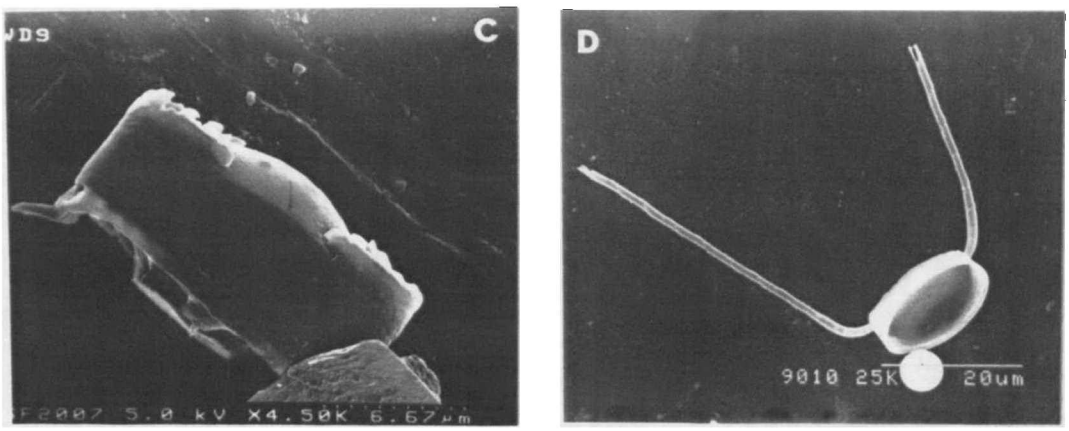
d Cyst with setae intact (SEM)

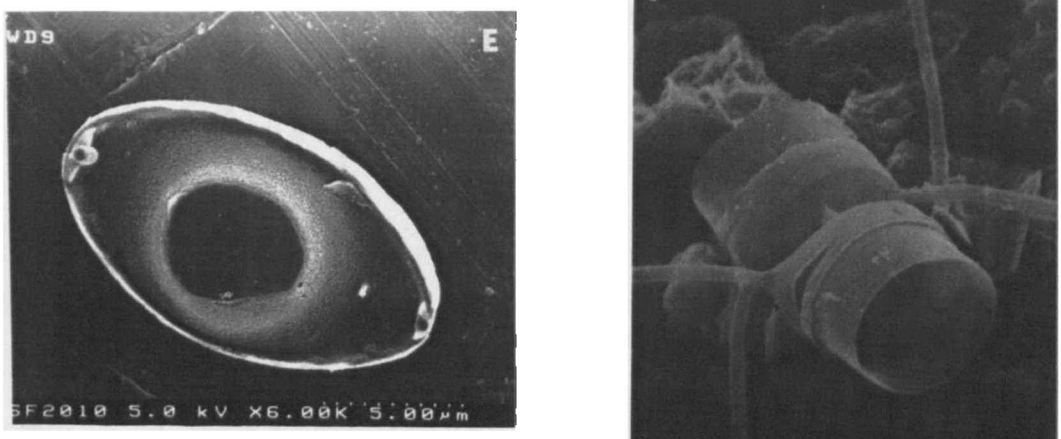
e Cyst without setae (SEM)

f Cyst with setae (SEM)

A1.6 a–f


A
B


WD9
C
SF2007 5.0 kV X4.50K 6.67µm
D
9010 25K 20µm


WD9
E
SF2010 5.0 kV X6.00K 5.00µm
F

Appendix 1 - Figure A1.7

***Cocconeis placentula* var *euglypta*, rapheless valve**

a Dissolution stage 1 assemblage (LM). Scale bar = 20 µm

b Dissolution stage 1, external view (SEM)

c Dissolution stage 1, internal view (SEM)

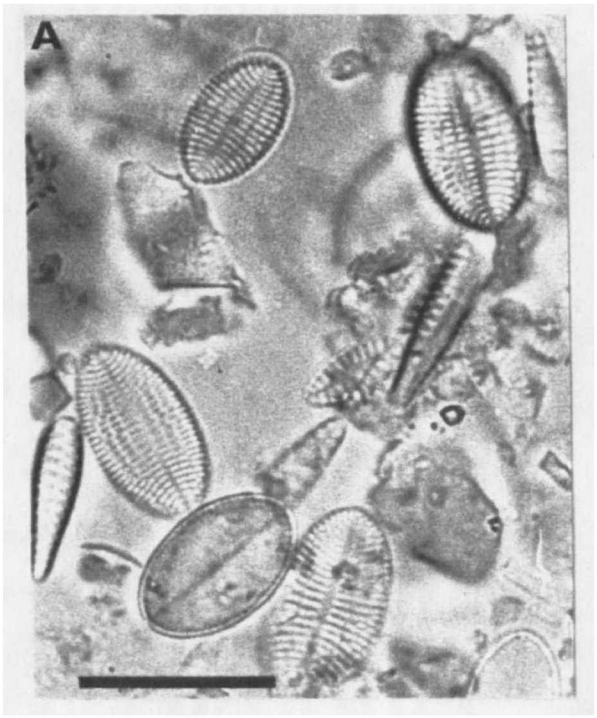
d Dissolution stage 1, internal view (SEM)

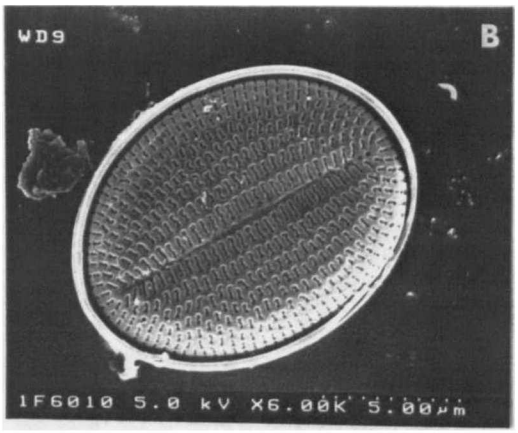
e Dissolution stage 1, with breakage (LM). Scale bar = 10 µm

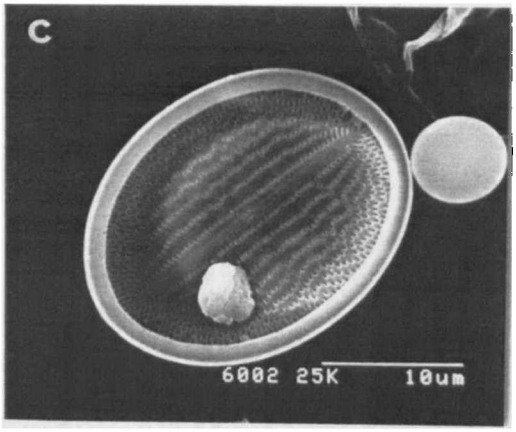
f Dissolution stage 2 (SEM)

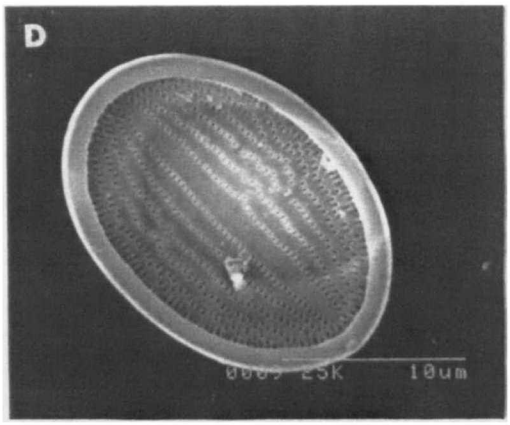
g Dissolution stage 2 (LM). Scale bar = 5 µm

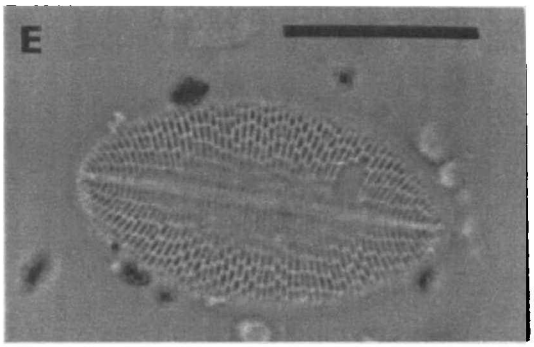
A1.7 a–g

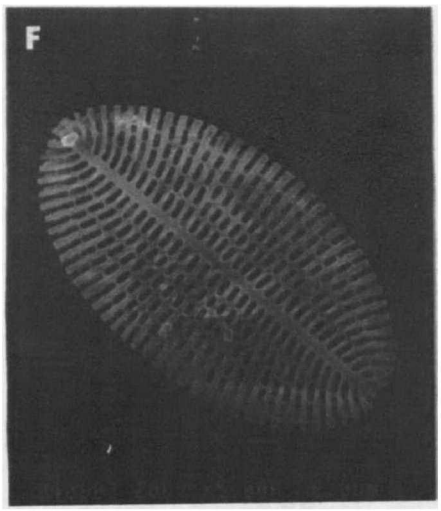


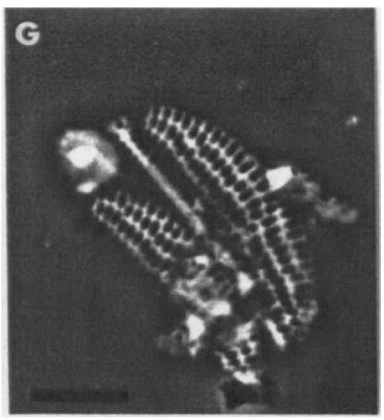












Appendix 1 - Figure A1.8

***Cocconeis placentula* var *euglypta*, raphe valve**

a Dissolution stage 1 (LM). Scale bar = 5 μm

b Dissolution stage 1 (SEM)

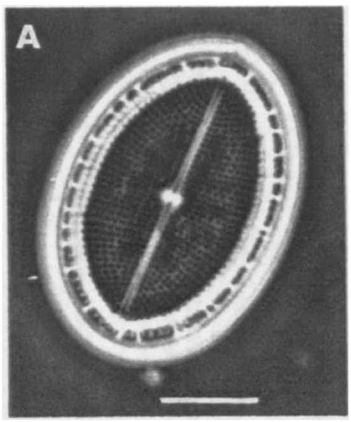
c Dissolution stage 1 (SEM)

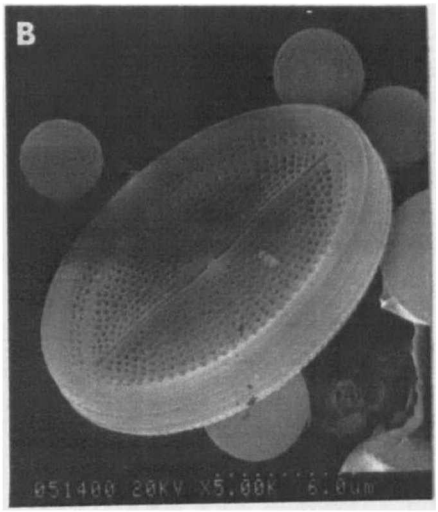
d Dissolution stage 1 with signs of areolae enlargement (SEM)

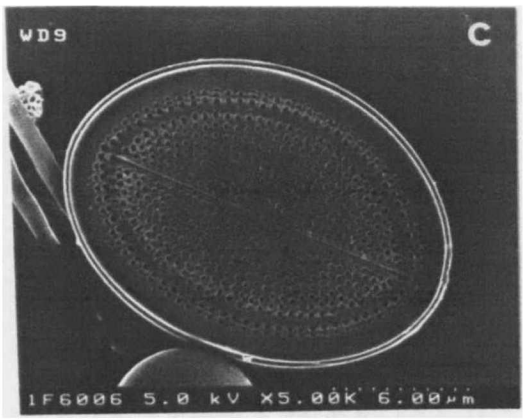
e Dissolution stage 2 (SEM)

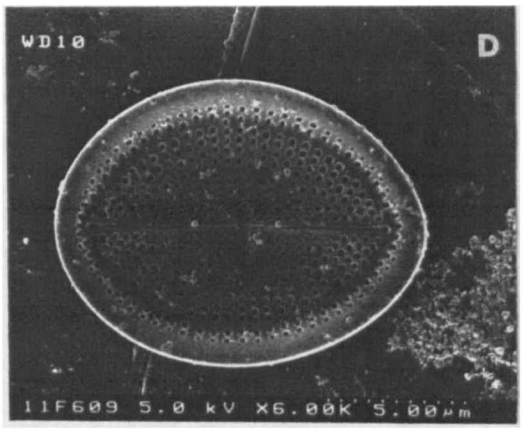
f Mantle separated from valve during dissolution (SEM)

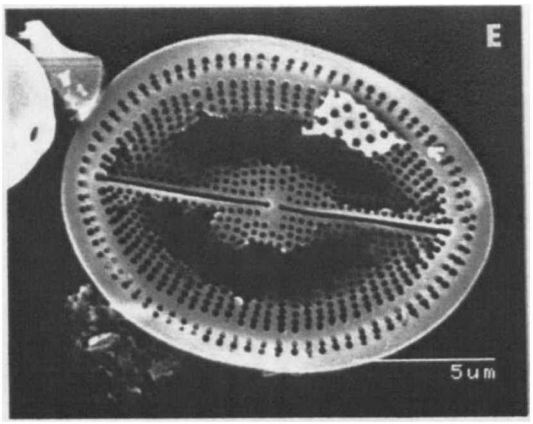
A1.8 a–f

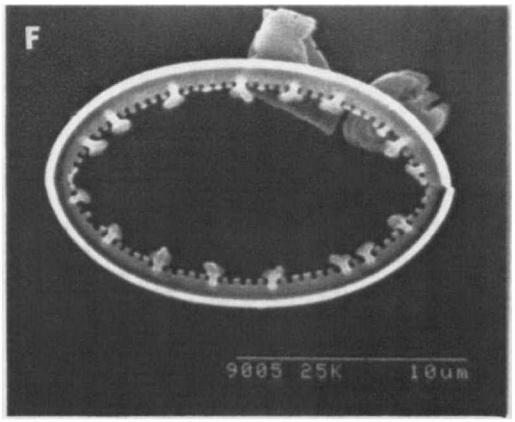

A


B
051400 20KV X5.00K 6.0um


WD9
C
1F6006 5.0 kV X5.00K 6.00µm


WD10
D
11F609 5.0 kV X6.00K 5.00µm


E
5um


F
9005 25K 10um

Appendix 1 - Figure A1.9

***Cocconeis pediculus*, rapheless valve**

a Dissolution stage 1 (LM). Scale bar = 5 µm

b Dissolution stage 1 (LM). Scale bar = 5 µm

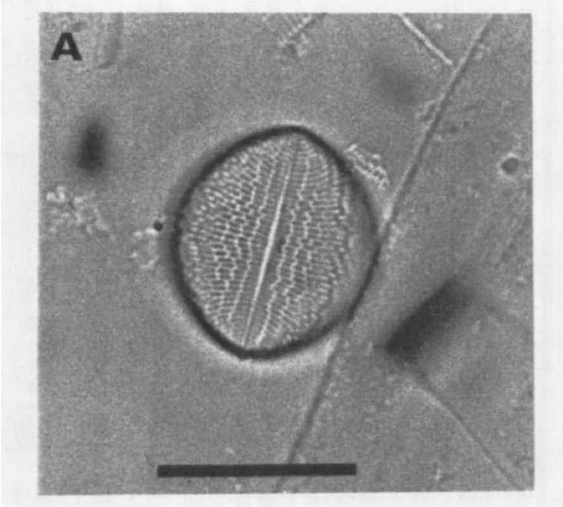
c Dissolution stage 1 (LM). Scale bar = 4 µm

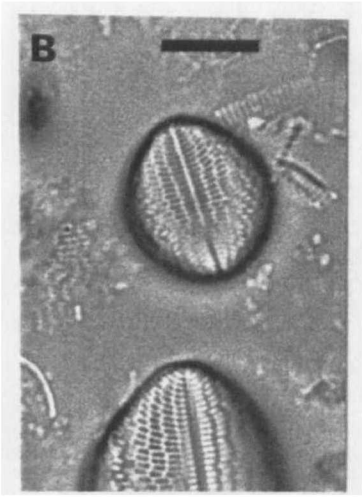
d Dissolution stage 1 (SEM)

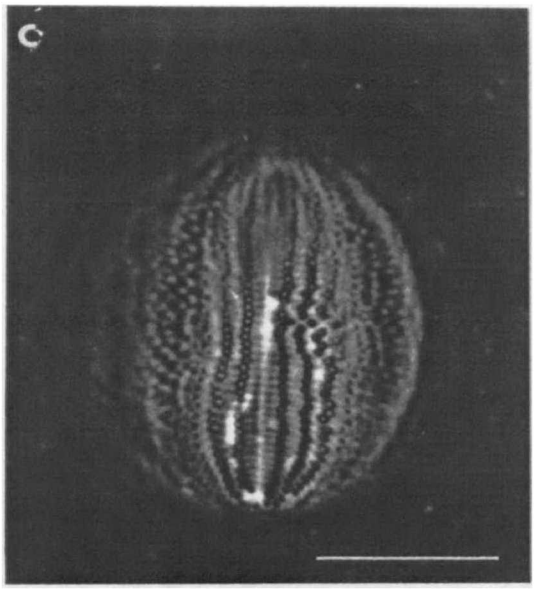
e Dissolution stage 1 (SEM)

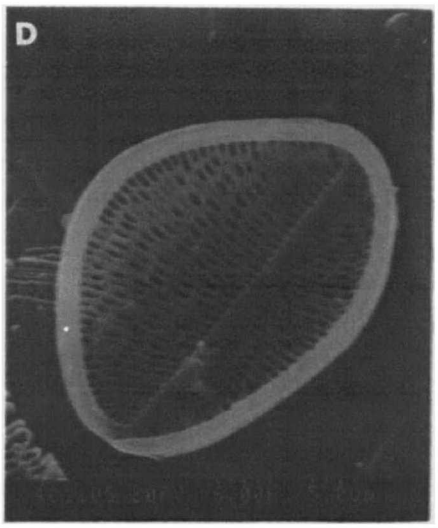
f Dissolution stage 2 (SEM)

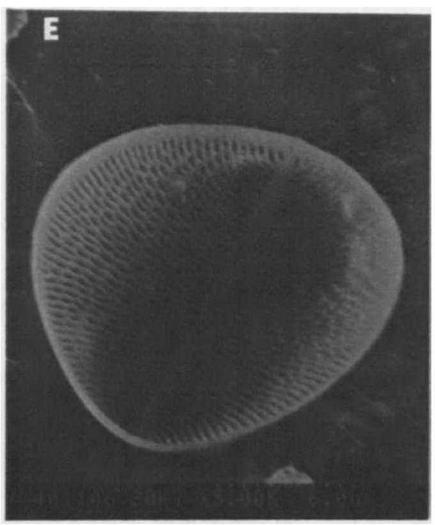
A1.9a–f

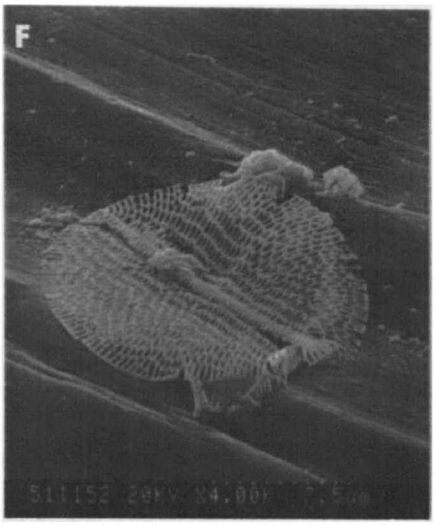












Appendix 1 - Figure A1.10

Cocconeis pediculus, raphe valve

a Dissolution stage 1 (LM). Scale bar = 5 μm

b Dissolution stage 1 (SEM)

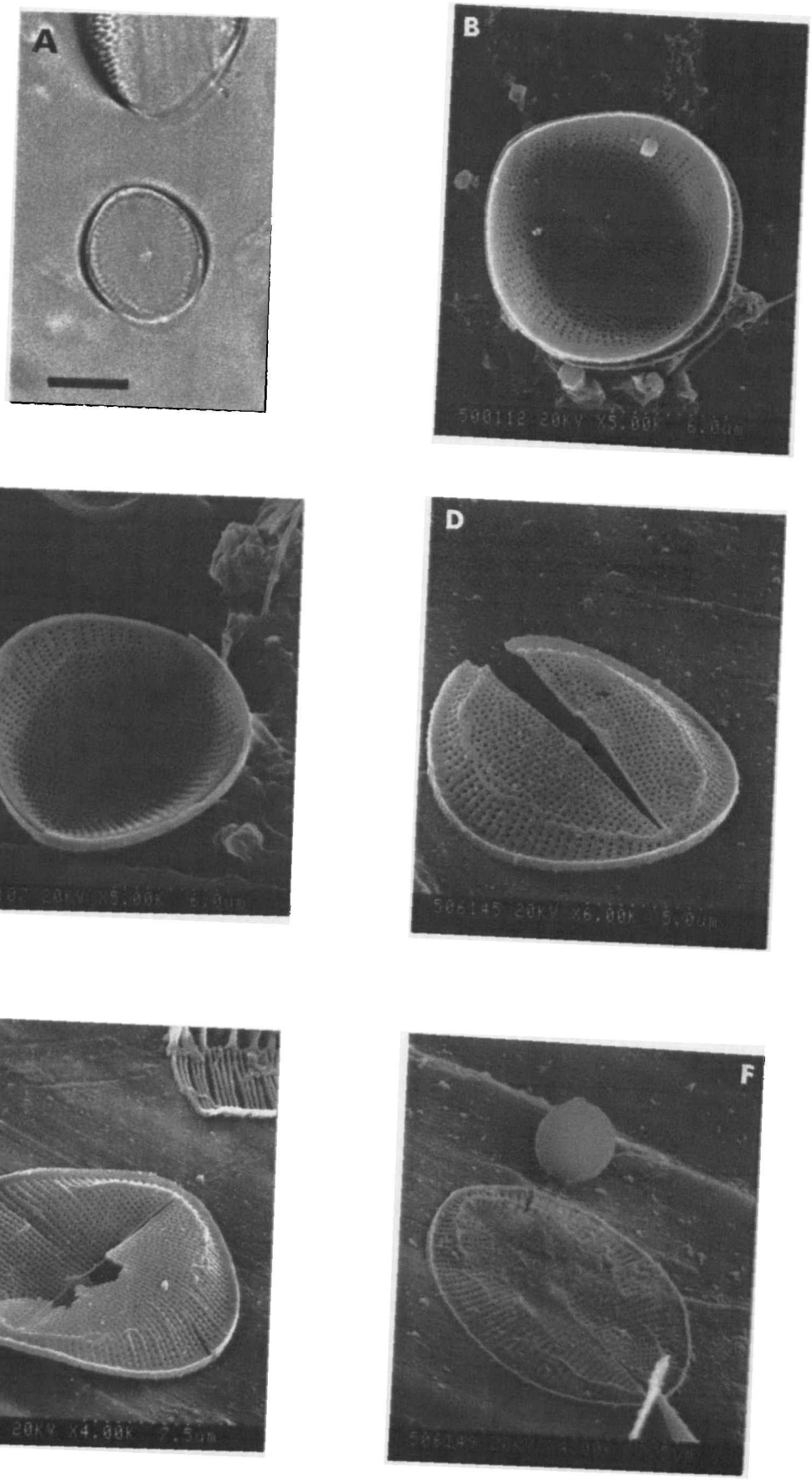
c Dissolution stage 1 (SEM)

d Dissolution stage 1 (SEM). Breakage is often initiated along the apical axis

e Dissolution stage 1 (SEM), as **d**

f Dissolution stage 2 (SEM)

A1.10 a f



Appendix 1 - Figure A1.11

Cyclotella caspia

a Dissolution stage 1 (LM). Scale bar = 5 µm

b Dissolution stage 1 (LM). Scale bar = 10 µm

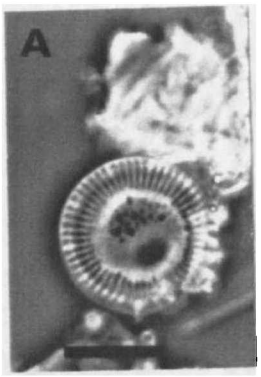
c Dissolution stage 1 (SEM)

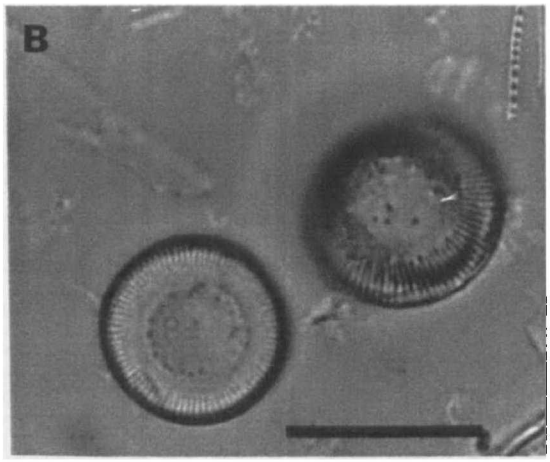
d Dissolution stage 1 (SEM)

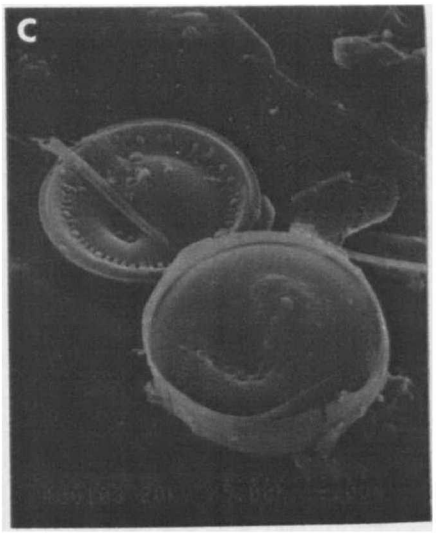
e Dissolution stage 3 (SEM)

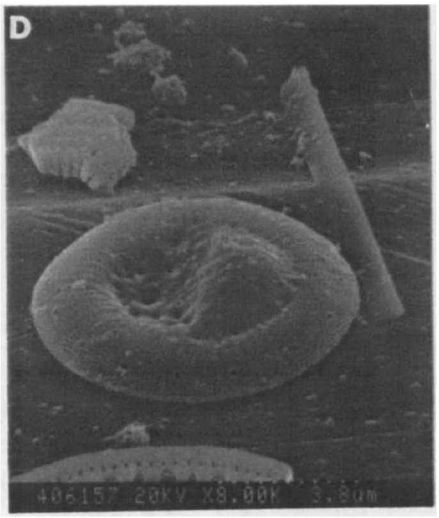
f Dissolution stage 3 (SEM)

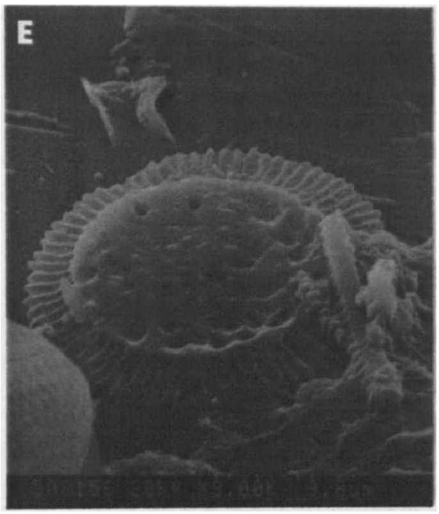
A1.11 a–f

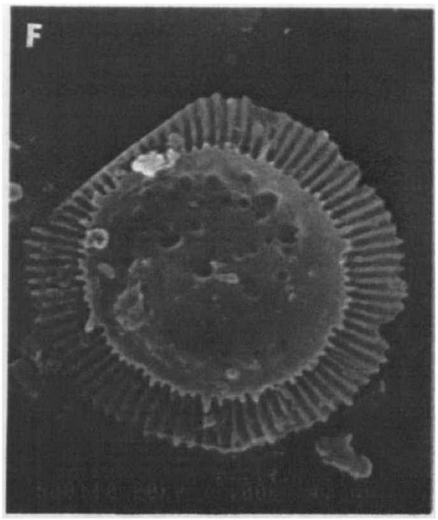












Appendix 1 - Figure A1.12

Cyclotella meneghiniana

a Dissolution stage 1 (LM). Scale bar = 8 µm

b Dissolution stage 1 (SEM). Detail shows structure of process (internal view)

c Dissolution stage 2 (SEM), with the outer margin complete

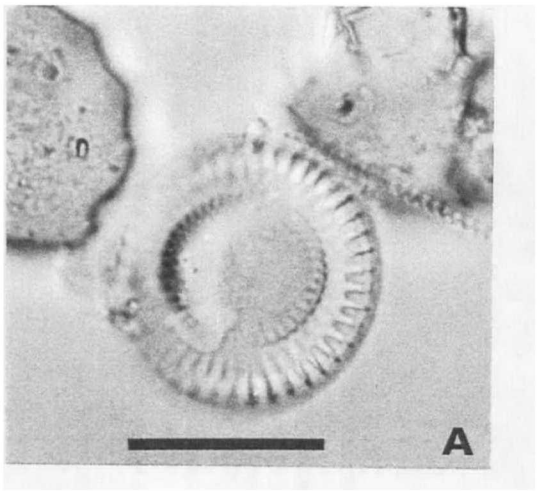
d Dissolution stage 3 (SEM), wit outer ring absent, but costae intact

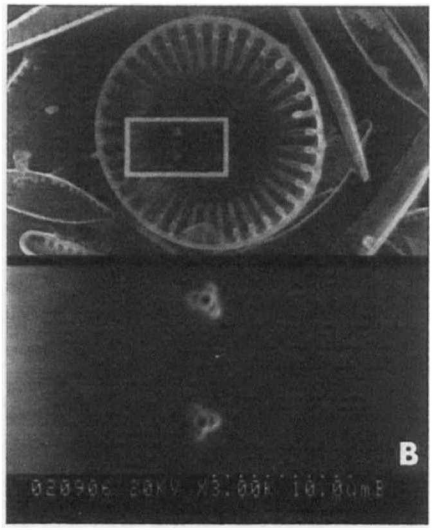
e Dissolution stage 3 (SEM)

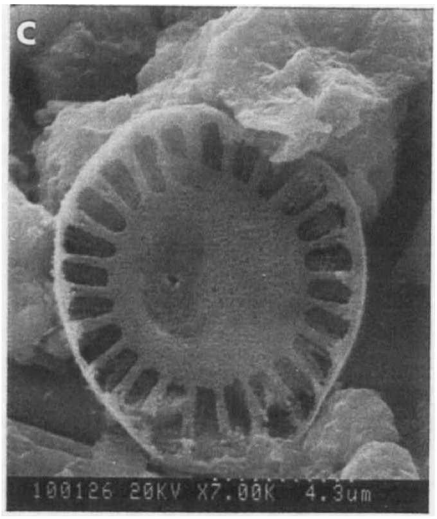
f Dissolution stage 3 (LM). Scale bar = 4 µm

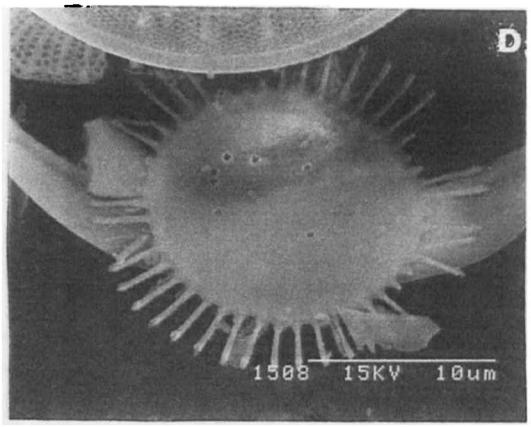
g Dissolution stage 4 (SEM). Only silica disc remains

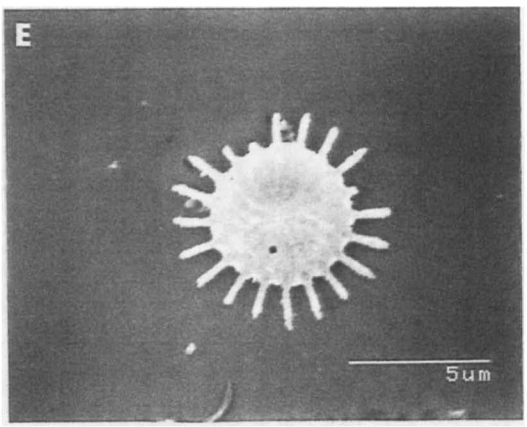
A1.12 a-g

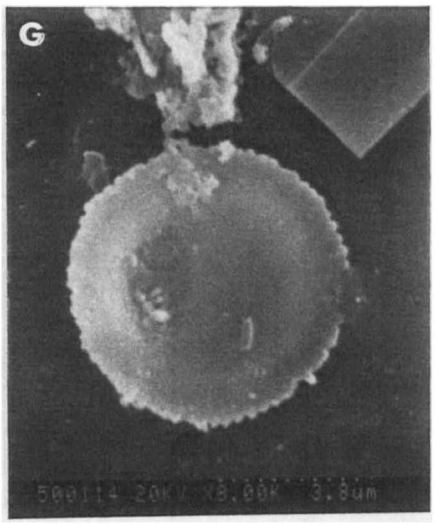


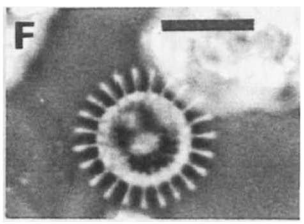












Appendix 1 - Figure A1.13

Cyclotella quillensis

a Fresh plankton sample, dissolution stage 1 (LM) - focus A. Scale bar = 20 μm

b Fresh plankton sample, dissolution stage 1 (LM) - focus A, showing valvar undulation. Scale bar = 20 μm

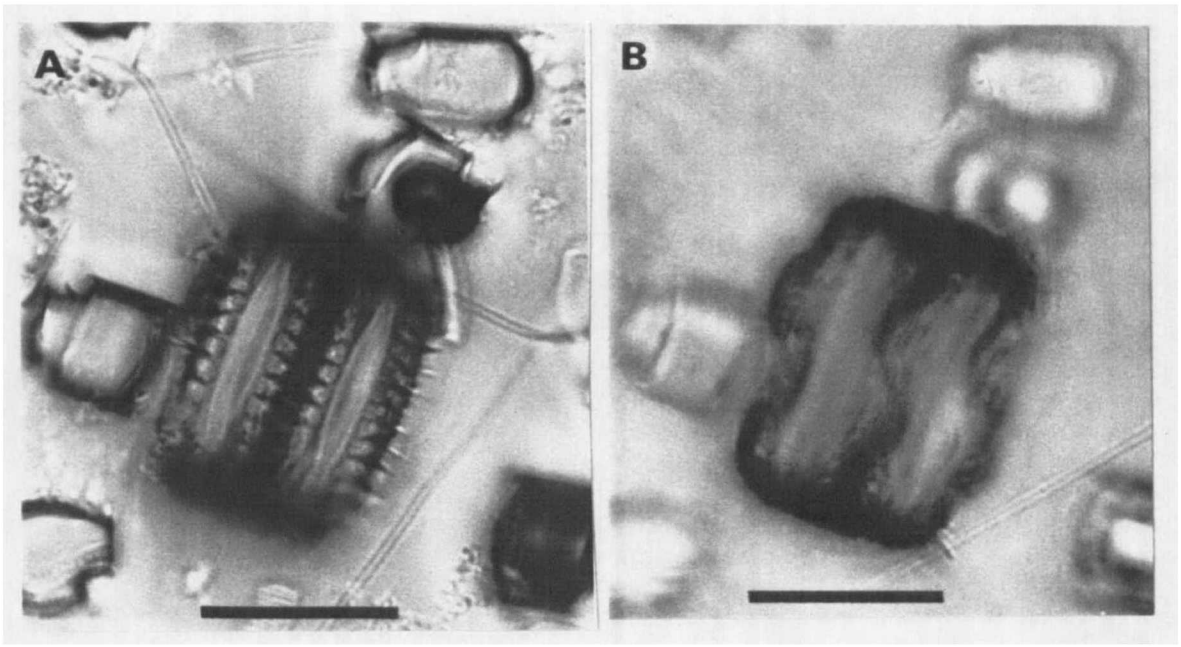
c Dissolution stage 3 (LM) - focus A. Scale bar = 10 μm

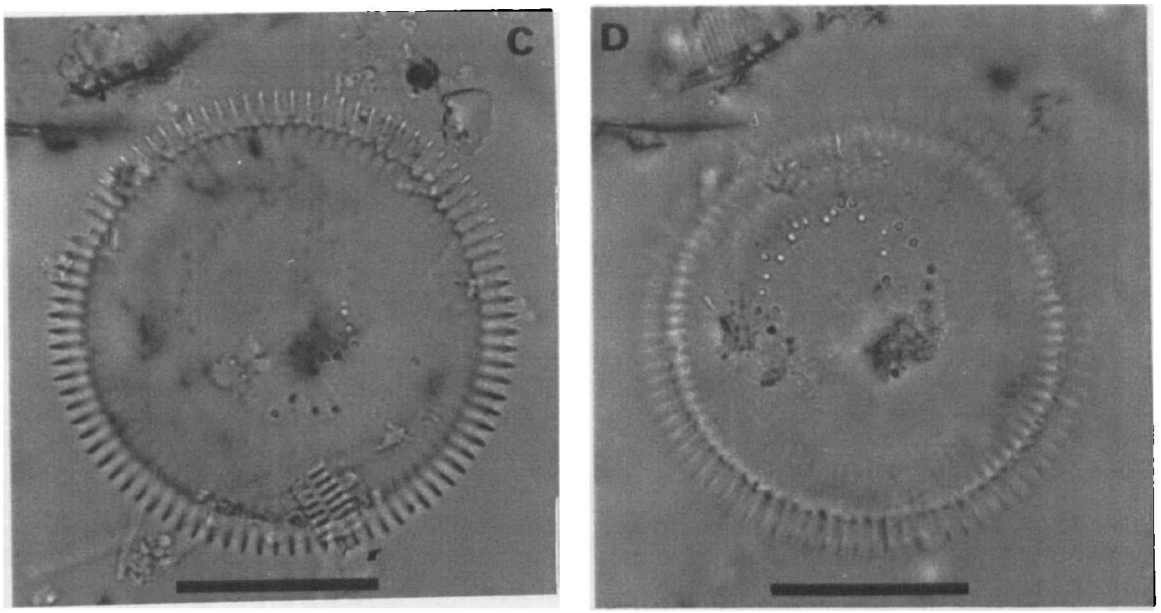
d Dissolution stage 3 (LM) - focus B. Scale bar = 10 μm

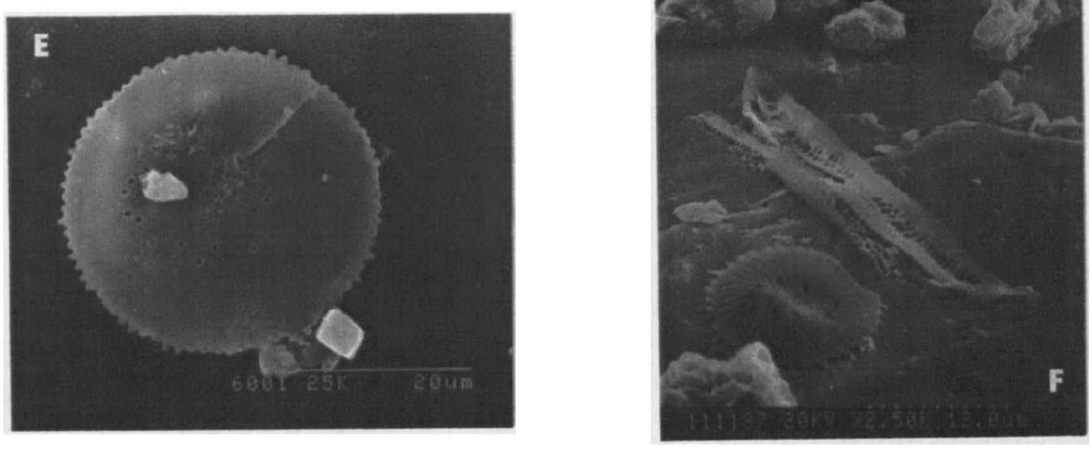
e Dissolution stage 4 (SEM)

f Dissolution stage 4 (SEM), with stage 3 for *Amphora libyca*

A1.13 a – f







Appendix 1 - Figure A1.14

Cymbella pusilla **(a-d) and** ***Cy. cistula*** **(e & f)**

a Fresh plankton sample, dissolution stage 1 (LM). Scale bar = 10 µm

b Dissolution stage 1, external view (SEM)

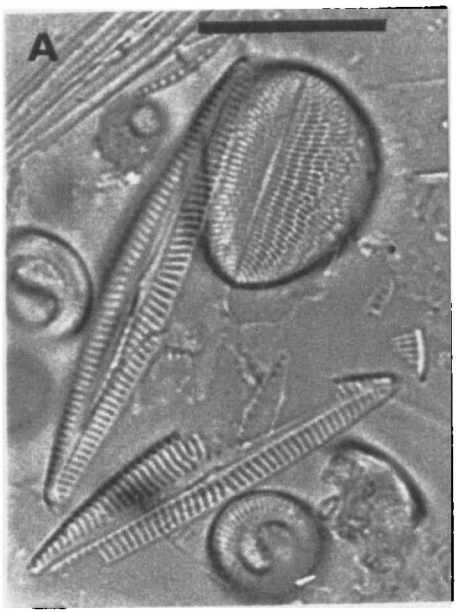
c Dissolution stage 1 (SEM), with some dissolution of internal structures (detail)

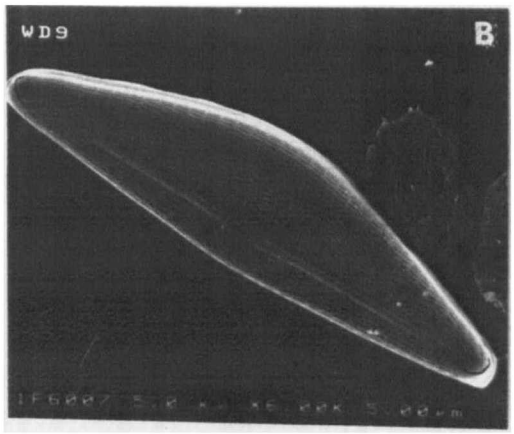
d Dissolution stage 2 (SEM), with apical degradation

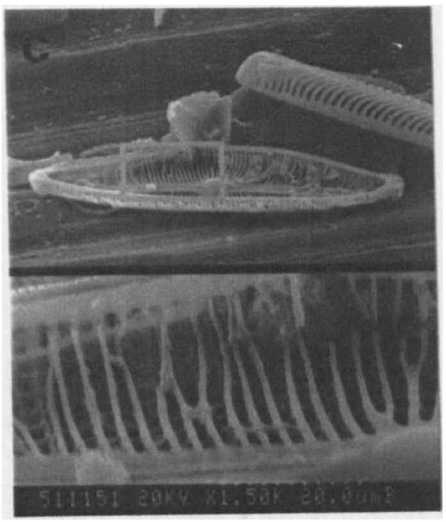
e Dissolution stage 1 (SEM)

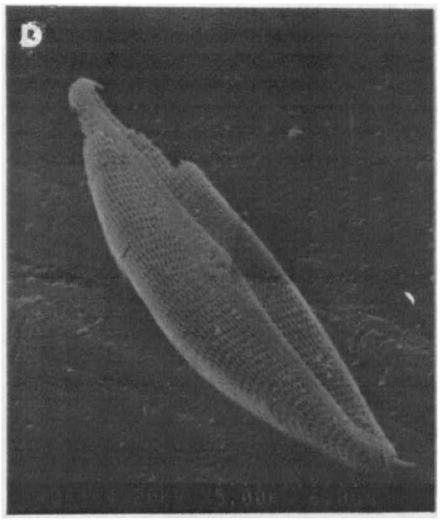
f Dissolution stage 3 (SEM)

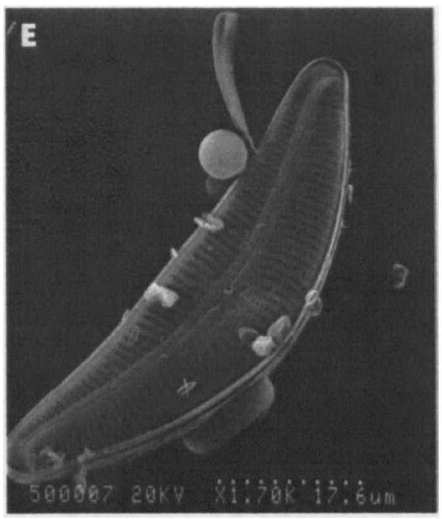
A1.14 a f

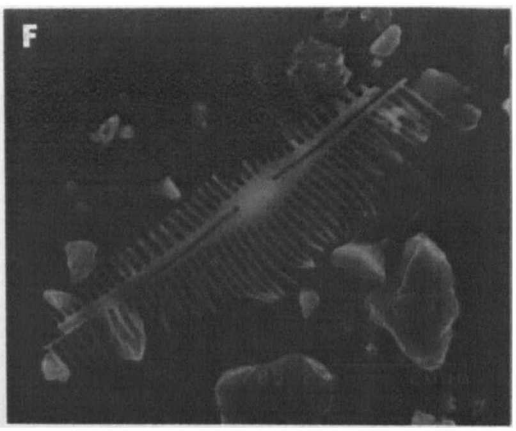












Appendix 1 - Figure A1.15

Mastogloia elliptica var ***dansei*** **(a-e) and** ***Ma. smithii*** var ***lacustris*** **(f & g)**

a Dissolution stage 1 (LM) - focus A. Scale bar = 12 µm

b Dissolution stage 1 (LM) - focus B. Scale bar = 12 µm

c Dissolution stage 2 (LM). Scale bar = 12 µm

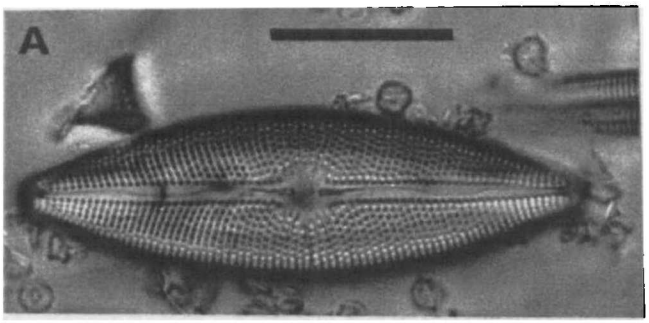
d Dissolution stage 3 (SEM)

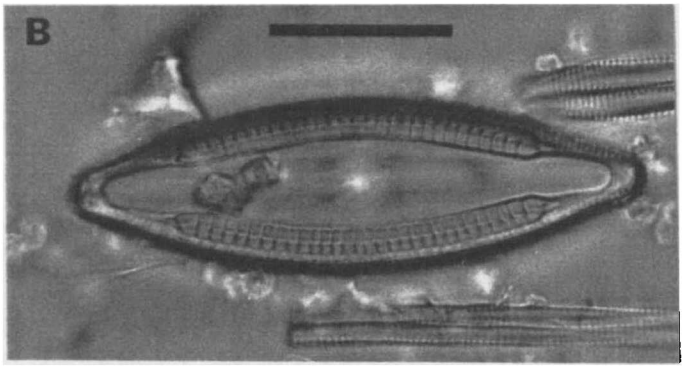
e Dissolution stage 4 (SEM). Only the distinctive central area remains

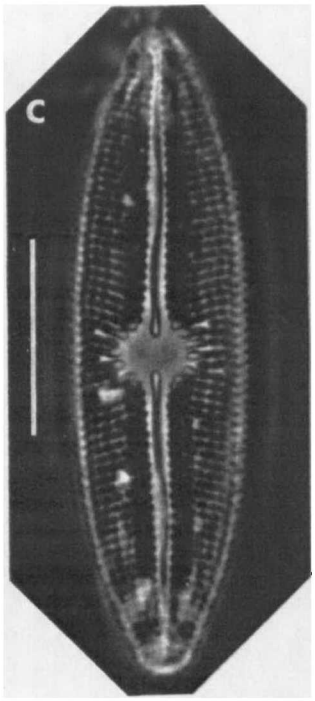
f Dissolution stage 1 (SEM)

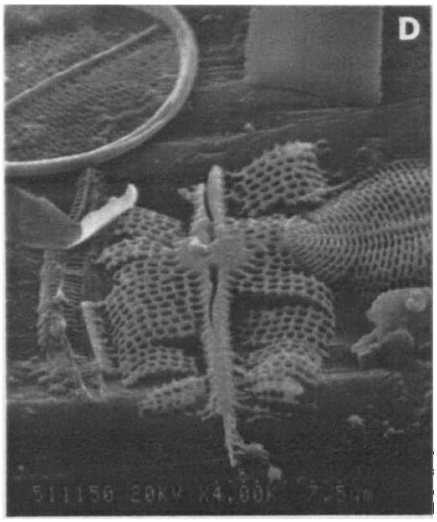
g Dissolution stage 2 (SEM)

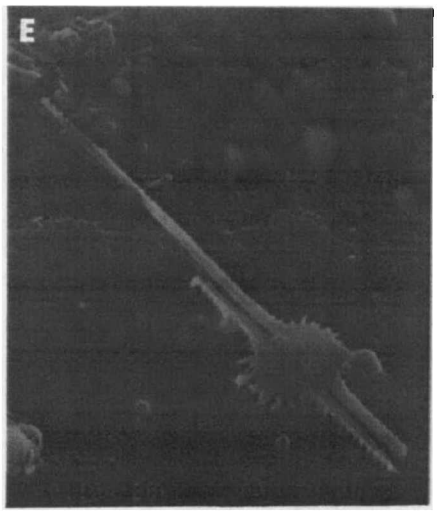
A1.15a–g

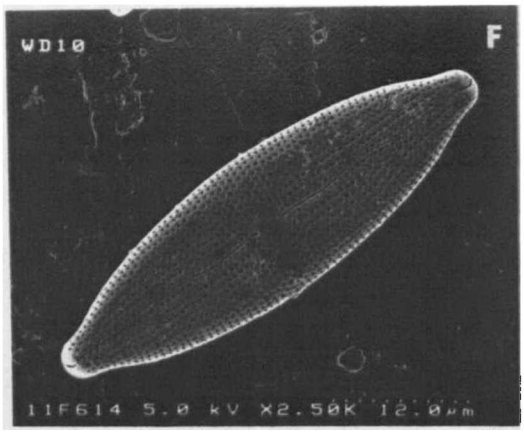


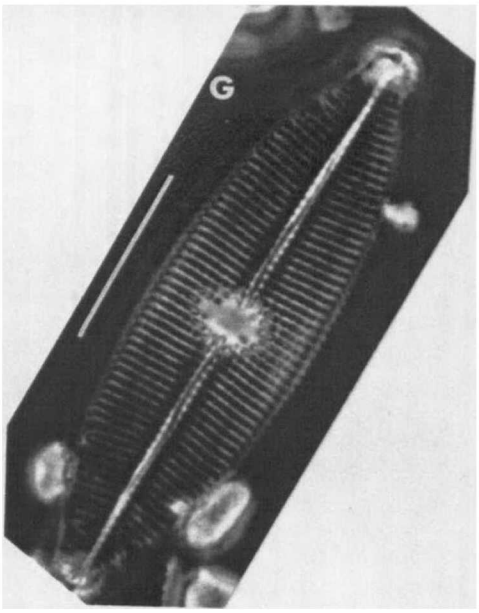












Appendix 1 - Figure A1.16

Navicula oblonga

a Dissolution stage 1 (SEM)

b Dissolution stage 2 (SEM)

c Dissolution stage 2 (SEM), detail of **b**

d Dissolution stage 2 (SEM), with detail of striae dissolution of internal structures

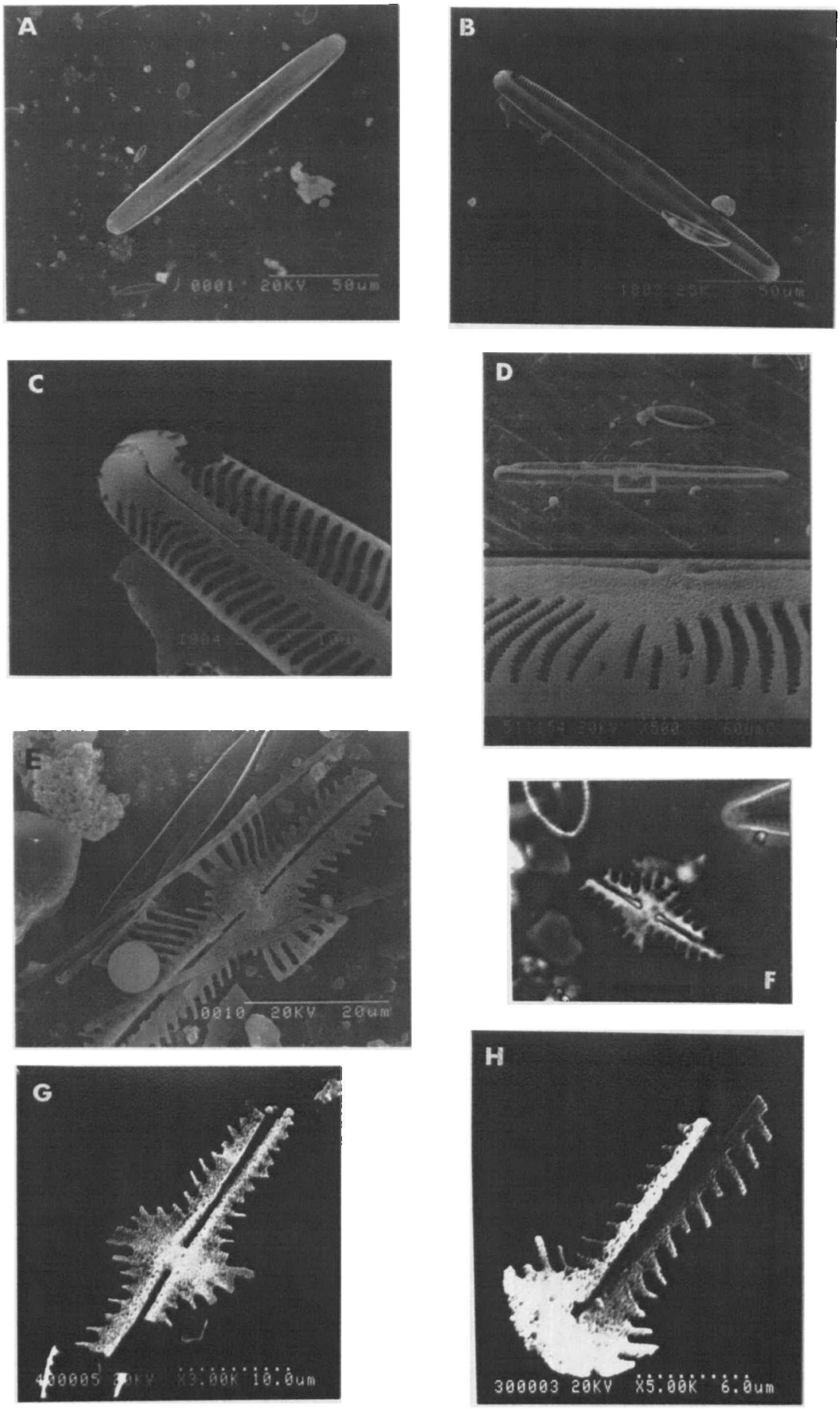
e Dissolution stage 3 (SEM). Dissolution proceeds from the apices to the central area

f Dissolution stage 4 (LM). Scale bar = 10 µm

g Dissolution stage 4 (SEM)

h Dissolved apical area, not used in counting (SEM)

A1.16a–h


A
0001 20KV 50um
B
C
D
E
0010 20KV 20um
F
G
H
300003 20KV X5.00K 6.0um

Appendix 1 - Figure A1.17

Nitzschia palea **(a, g & f) and** ***Ni. frustulum*** **(b, c, d, e & h)**

a Dissolution stage 1 (LM). Scale bar = 10 μm

b Dissolution stage 1 (LM). Scale bar = 3 μm

c Dissolution stage 1 (LM). Scale bar = 5 μm

d Dissolution stage 1 (SEM)

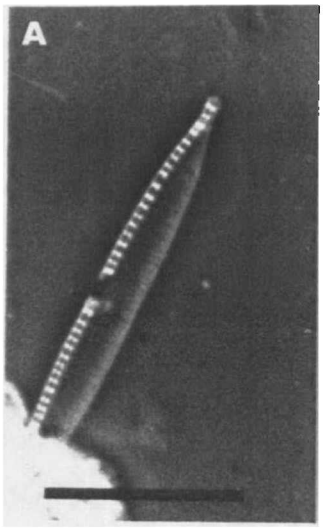
e Dissolution stage 1 (SEM)

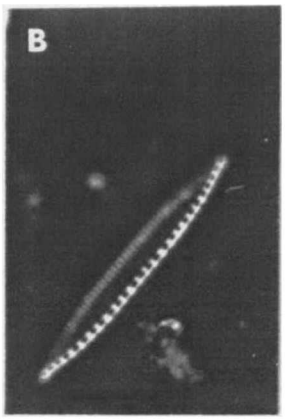
f Detail of valve dissolution (SEM)

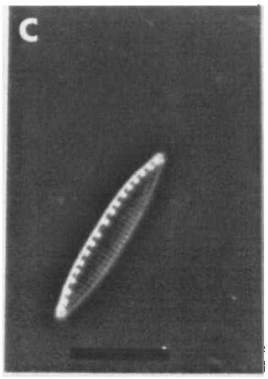
g Dissolution stage 2 (SEM)

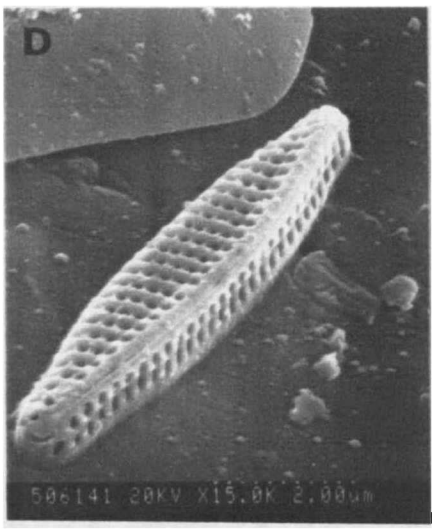
h Dissolution stage 2 (SEM)

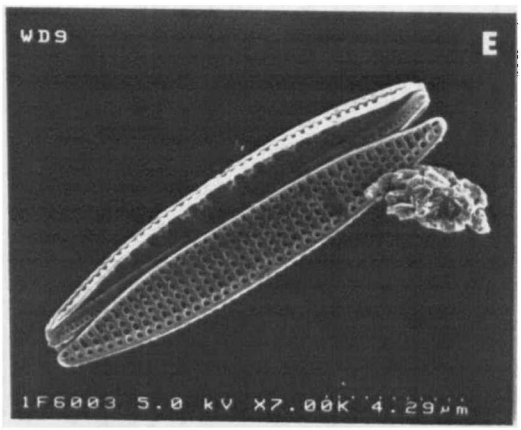
A1.17a – h

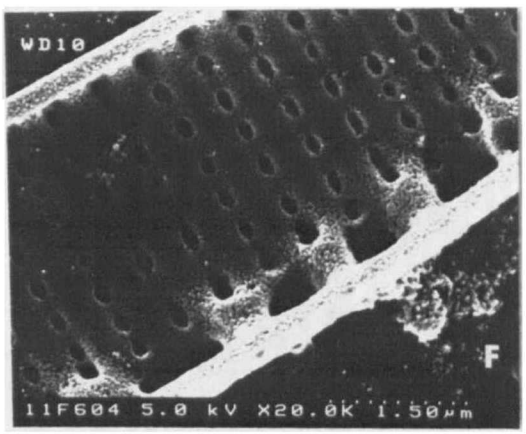

A

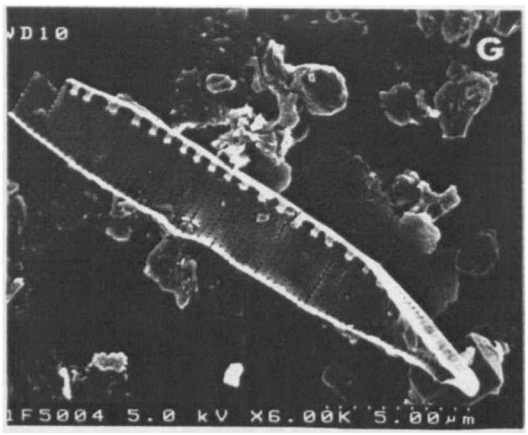

B

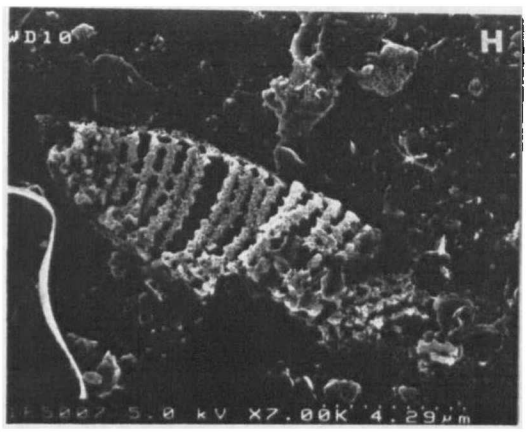

C


D
506141 20KV X15.0K 2.00µm


WD9
E
1F6003 5.0 kV X7.00K 4.29µm


WD10
F
11F604 5.0 kV X20.0K 1.50µm


WD10
G
1F5004 5.0 kV X6.00K 5.00µm


WD10
H
5.0 kV X7.00K 4.29µm

Appendix 1 - Figure A1.18

Rhoicosphenia curvata and *Rhopalodia gibba*

a Dissolution stage 1 (LM), girdle view. Scale bar = 15 µm

b Dissolution stage 1 (SEM), whole cell in girdle view

c Dissolution stage 1 (SEM), rapheless valve

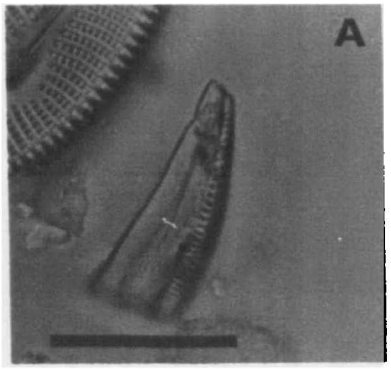
d Dissolution stage 2 (SEM), rapheless valve

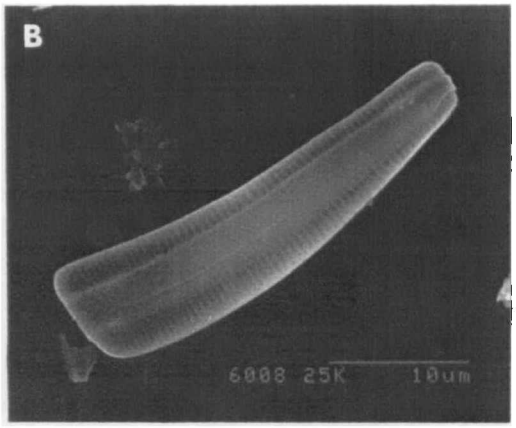
e Dissolution stage 1 (SEM)

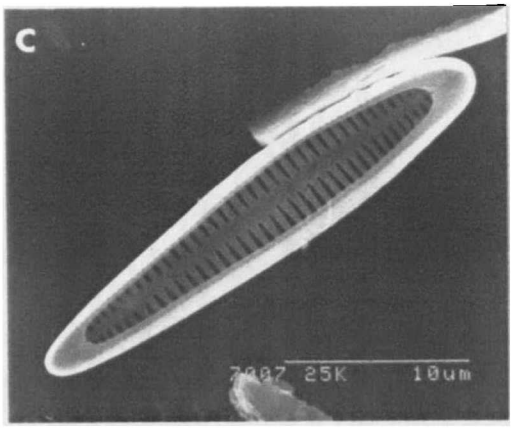
f Dissolution stage 2 (SEM), with loss of valve ends

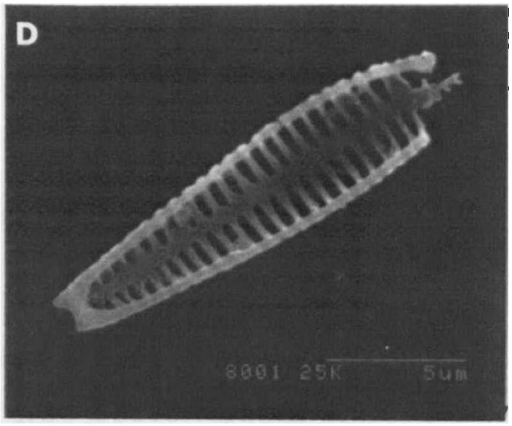
g Dissolution stage 1 (LM). Scale bar = 10 µm

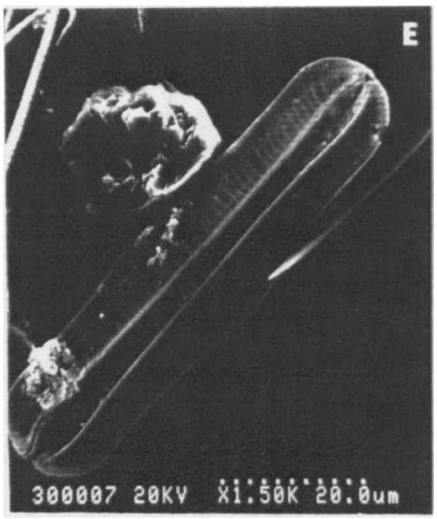
A1.18a g

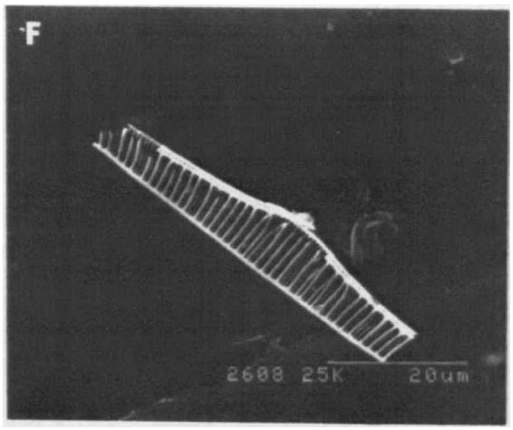

A

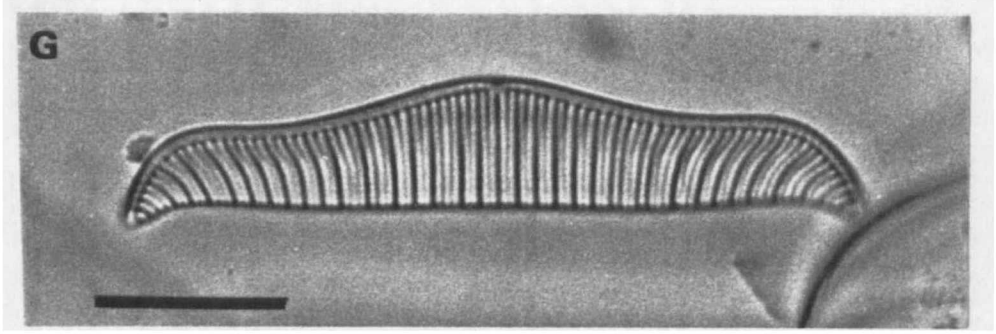

B
6008 25K 10um


C
7007 25K 10um


D
8001 25K 5um


E
300007 20KV X1.50K 20.0um


F
2608 25K 20um


G

Appendix 1 - Figure A1.19

Stephanodiscus minutulus

a Dissolution stage 1 (LM) - focus A. Scale bar = 3 µm

b Dissolution stage 1 (LM) - focus B. Scale bar = 3 µm

c Dissolution stage 1 (LM) - focus A. Scale bar = 3 µm

d Dissolution stage 1 (LM) - focus B. Scale bar = 3 µm

e Dissolution stage 1 (LM). Scale bar = 2 µm

f Dissolution stage 1 (SEM), external view

g Dissolution stage 1 (SEM), internal view

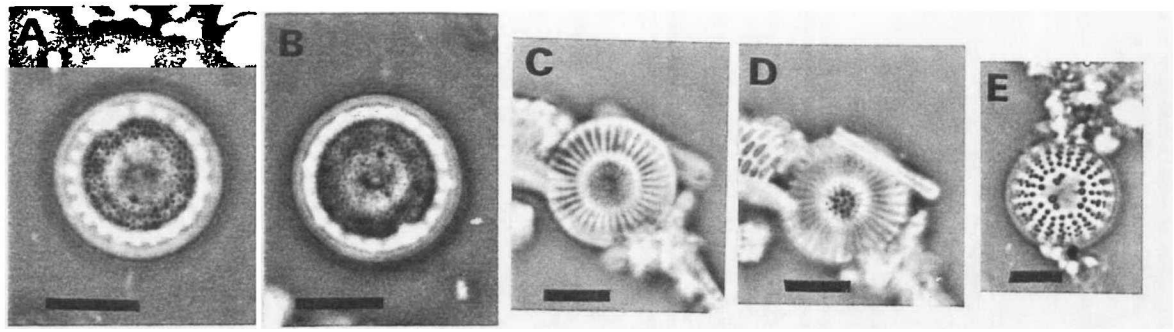
h Dissolution stage 1 (SEM), with some dissolution evident

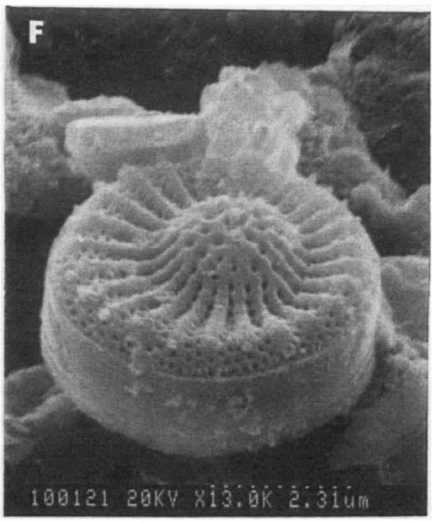
i Dissolution stage 2 (SEM), with vestigial marginal spines

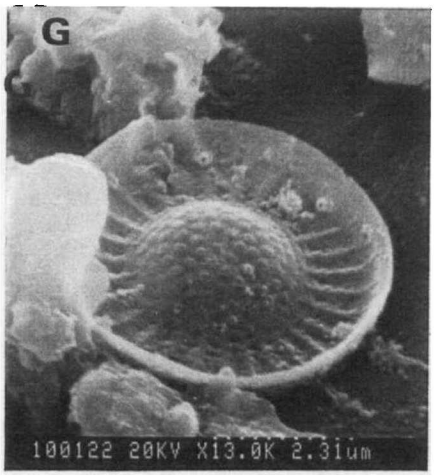
j Dissolution stage 2 (SEM), as **i**

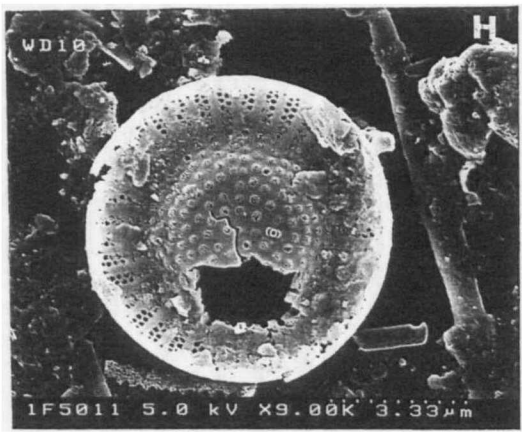
k Dissolution stage 3 (SEM), with complete loss of marginal spines

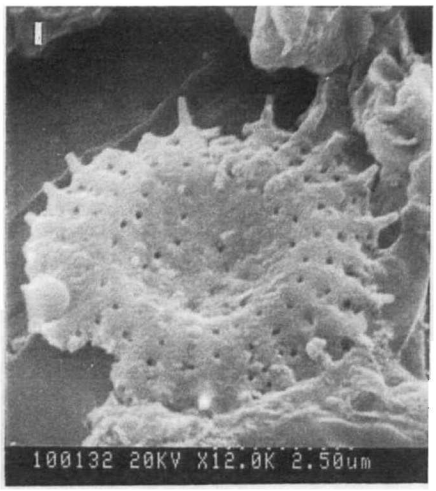
A1.19 a–k

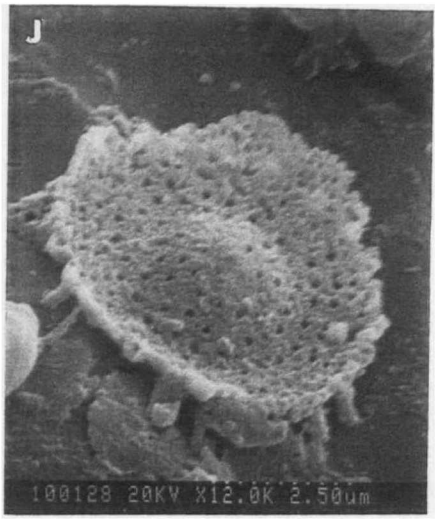

A
B
C
D
E

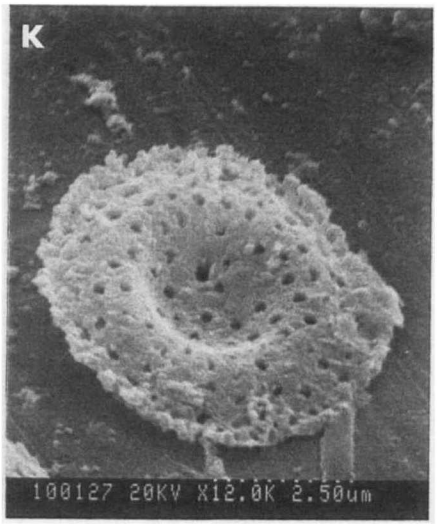

F
100121 20KV X13.0K 2.31um


G
100122 20KV X13.0K 2.31um


WD10
H
1F5011 5.0 kV X9.00K 3.33µm


I
100132 20KV X12.0K 2.50um


J
100128 20KV X12.0K 2.50um


K
100127 20KV X12.0K 2.50um

Appendix 1 - Figure A1.20

Stephanodiscus niagarae

a Dissolution stage 1 (LM). Scale bar = 8 µm

b Dissolution stage 1 (SEM), with some dissolution

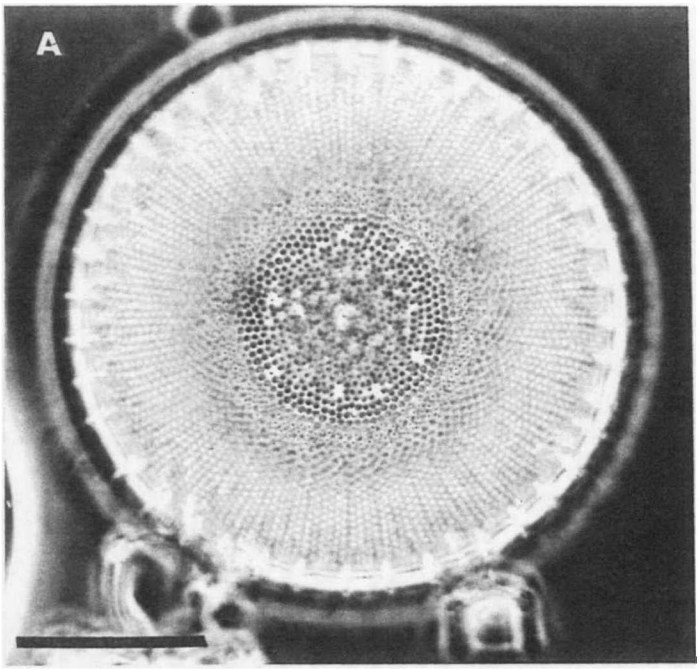
c Dissolution stage 1 (SEM), with detail of areolae (internal view)

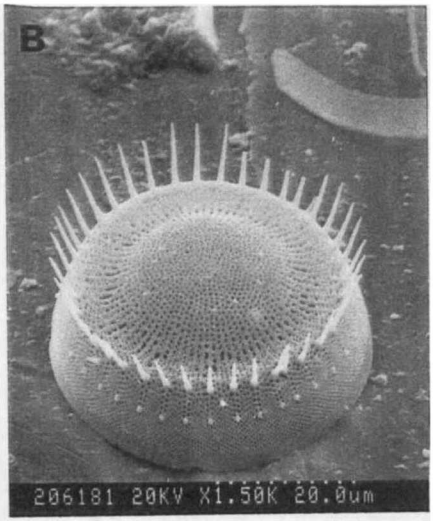
d Dissolution stage 2 (SEM), showing loss of structural integrity

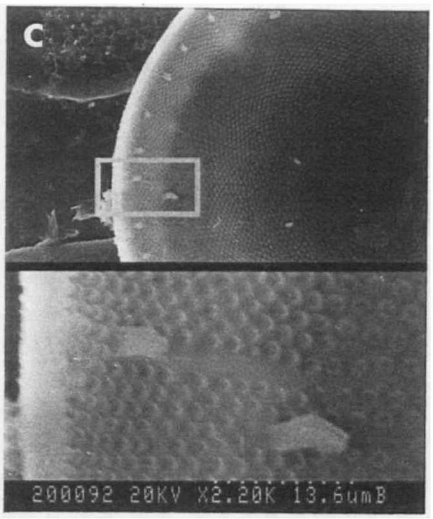
e Dissolution stage 3 (SEM). Note the loss of marginal spines (cf **b**)

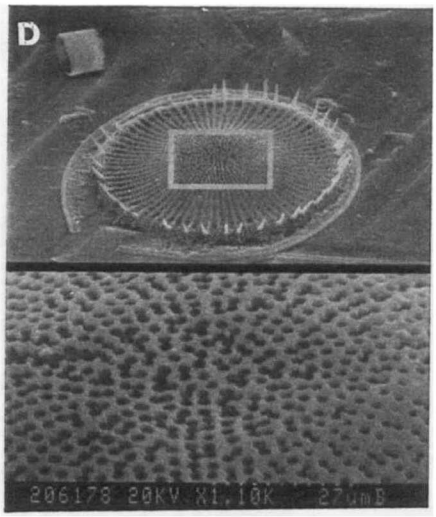
f Dissolution stage 3 (SEM); as **e**

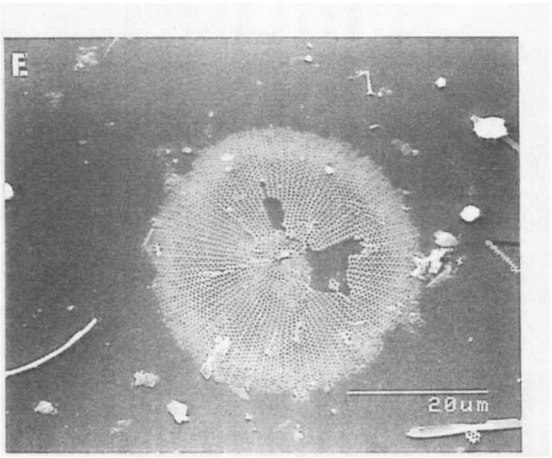
A1.20a–f

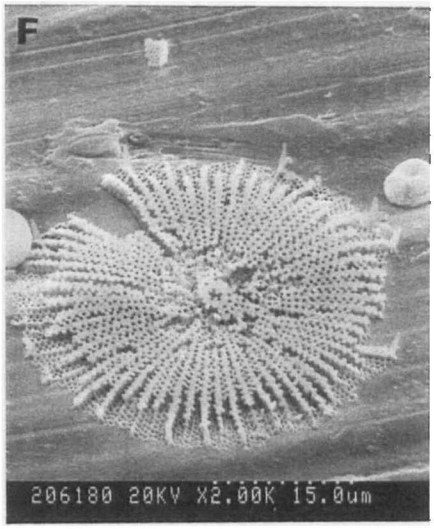

A


B
206181 20KV X1.50K 20.0um


C
200092 20KV X2.20K 13.6umB


D
206178 20KV X1.10K 27umB


E
20um


F
206180 20KV X2.00K 15.0um

Appendix 1 - Figure A1.21

Surirella ovalis

a Dissolution stage 1 (LM) - *focus* A. Scale bar = 20 μm

b Dissolution stage 1 (LM) - focus B. Scale bar = 20 μm

c Dissolution stage 1 (SEM), valve view

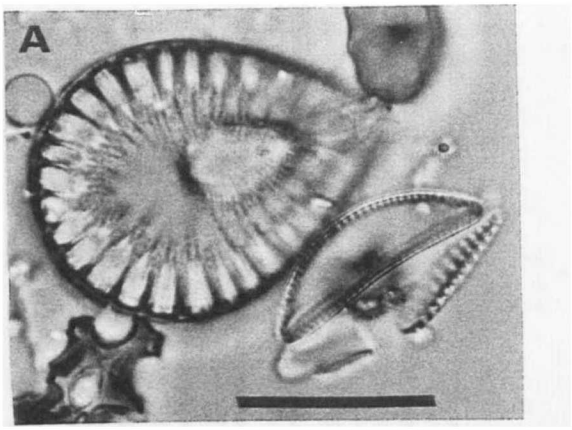
d Dissolution stage 1 (SEM), girdle view

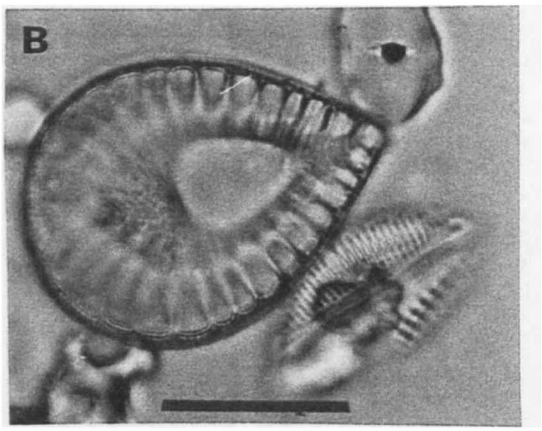
e Dissolution stage 2 (SEM), internal view. Note dissolution at valve edges

f Dissolution stage 2 (SEM), external view; as **e**

g Dissolution stage 3 (SEM), internal view. Note loss of intercostal areas of valve, and distinct margin

A1.21a–g


A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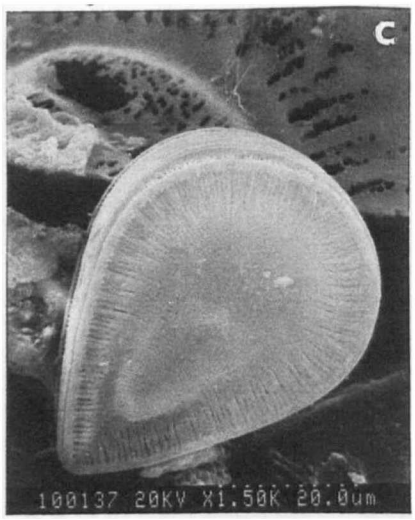
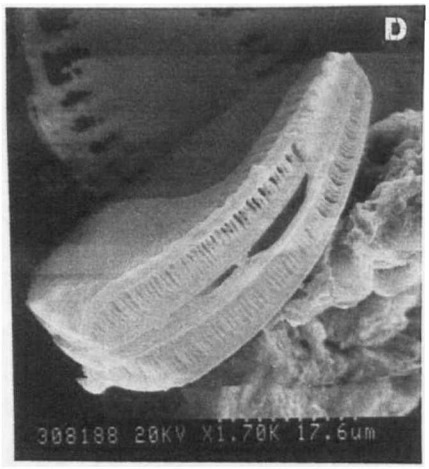
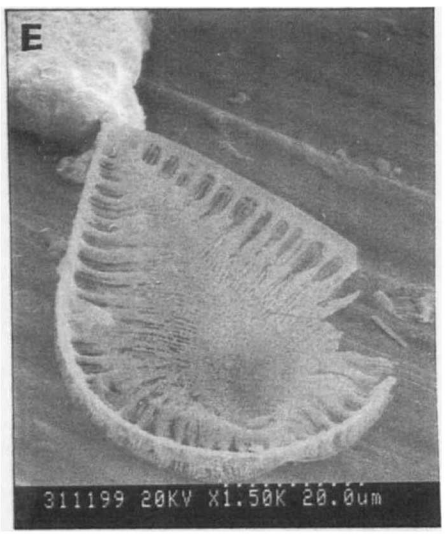

C
100137 20KV X1.50K 20.0um


D
308188 20KV X1.70K 17.6um


E
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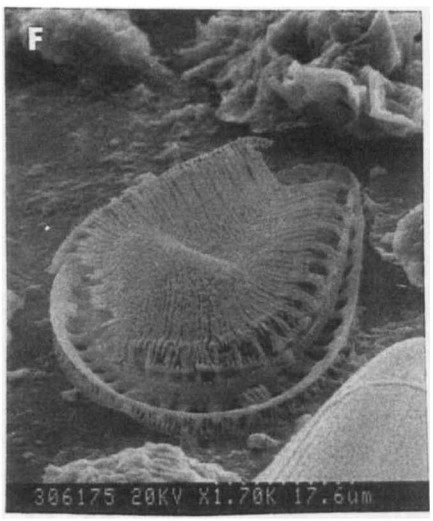
F
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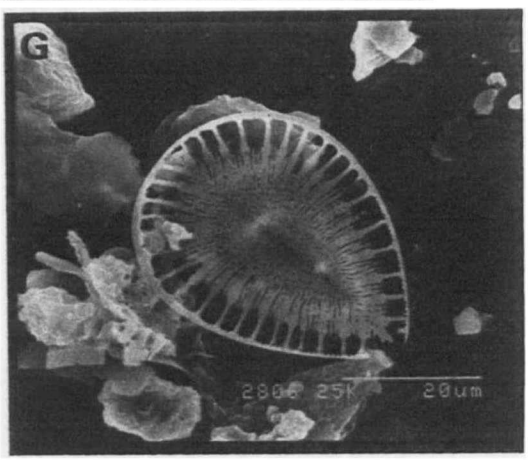

G
20um

Appendix 1 - Figure A1.22

Surirella striatula

a Dissolution stage 1 (LM). Scale bar = 30 μm

b Dissolution stage 1 (LM). Scale bar = 25 μm

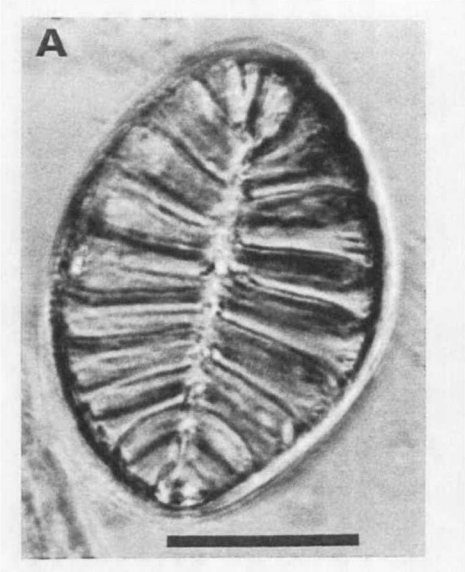
c Dissolution stage 1 (SEM)

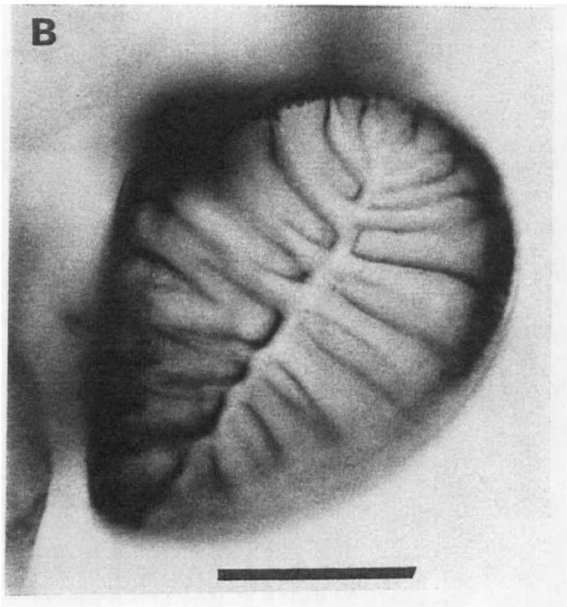
d Dissolution stage 2 (SEM), showing robust valve ribs and margin

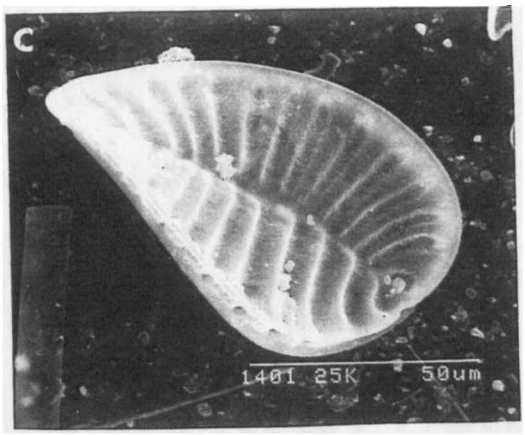
e Dissolution stage 2 (SEM), as **d**

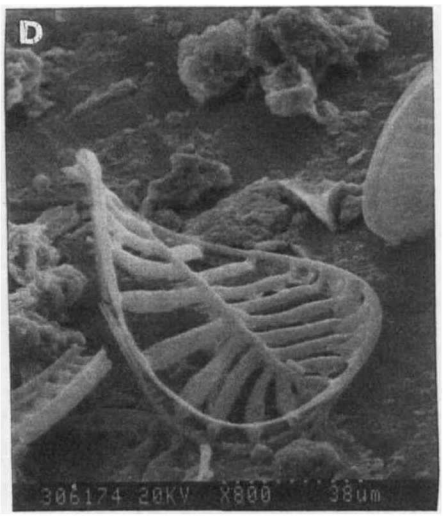
f Dissolution stage 3 (SEM). Marginal rim is progressively dissolved

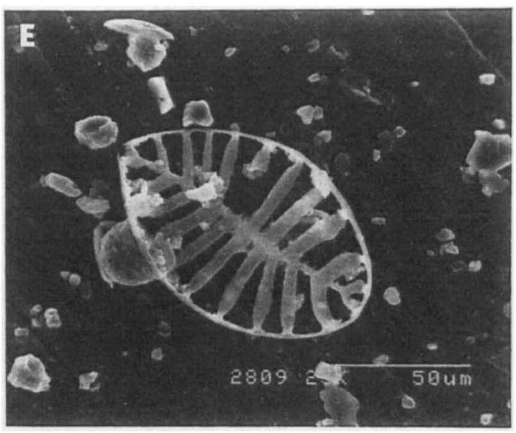
A1.22a–f

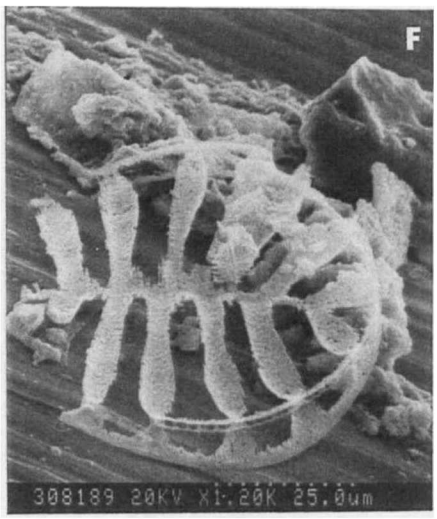

A


B


C
1401 25K 50um


D
306174 20KV X800 38um


E
2809 25K 50um


F
308189 20KV X1.20K 25.0um

Appendix 1 - Figure A1.23

***Synedra fasciculata* (a-e) & *Sy. pulchella* (f & g)**

a Dissolution stage 1 (SEM)

b Dissolution stage 2 (SEM) (see **d**)

c Dissolution stage 1 (SEM)

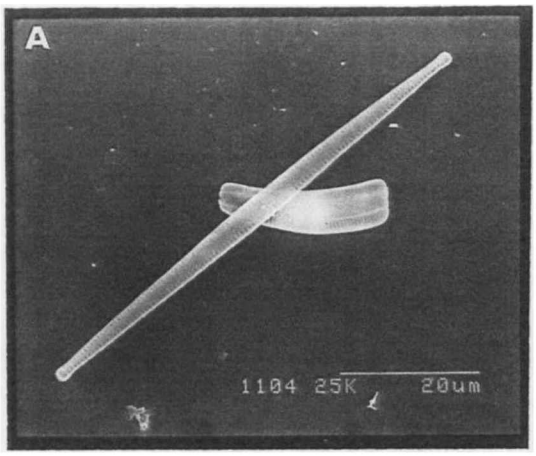
d Dissolution stage 2 (SEM), detail of **b**. Note dissolution of internal striae structure

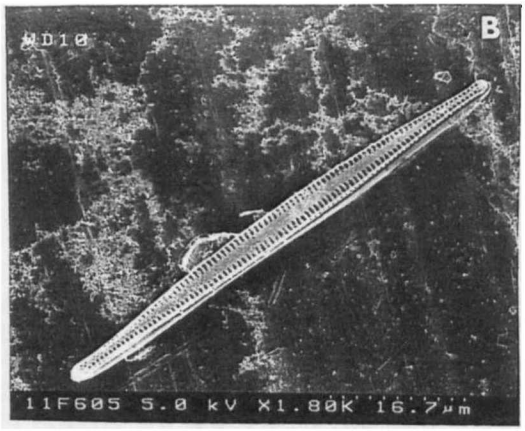
e Dissolution stage 2 (LM), as **d**. Scale bar = 10 μm

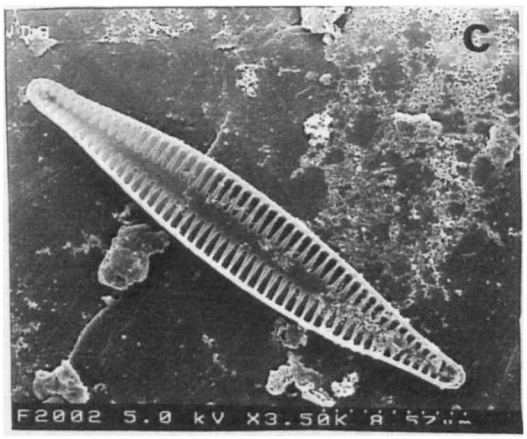
f Dissolution stage 1 (SEM)

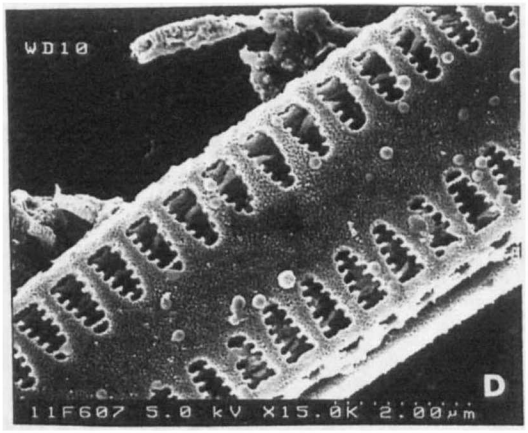
g Dissolution stage 3 (SEM). The central inflation of this taxon is a distinct "dissolution taxon"

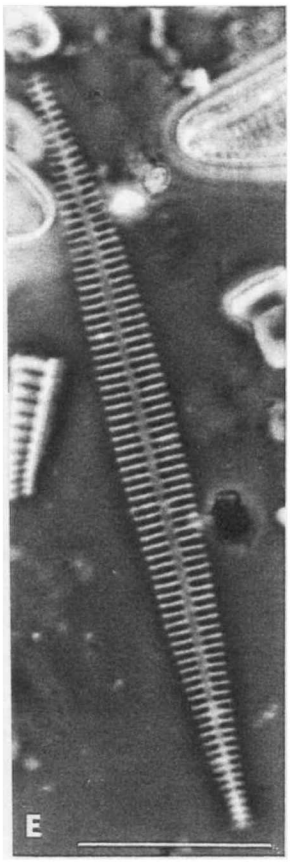
A1.23a–g


A
1104 25K 20um


WD10
B
11F605 5.0 kV X1.80K 16.7µm


C
F2002 5.0 kV X3.50K


WD10
D
11F607 5.0 kV X15.0K 2.00µm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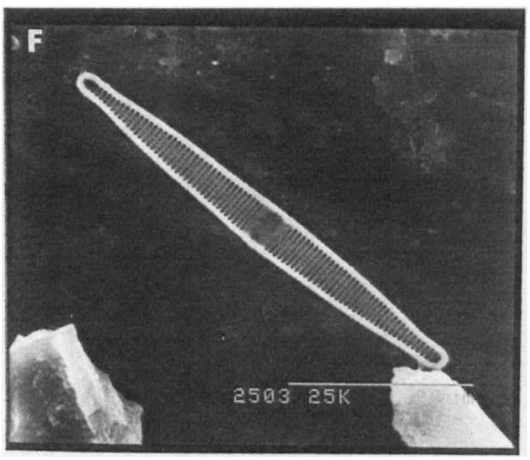
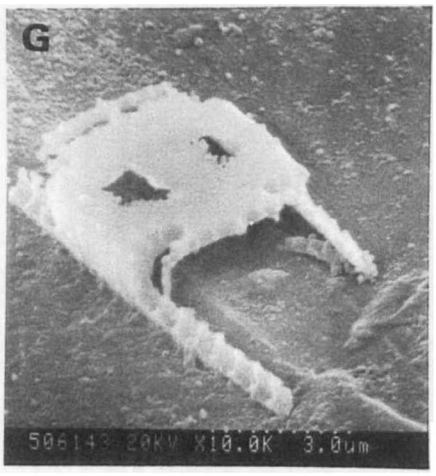
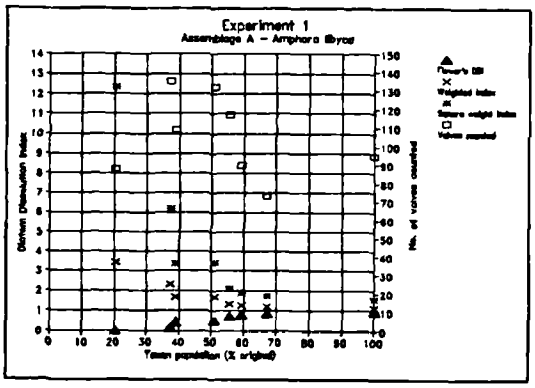
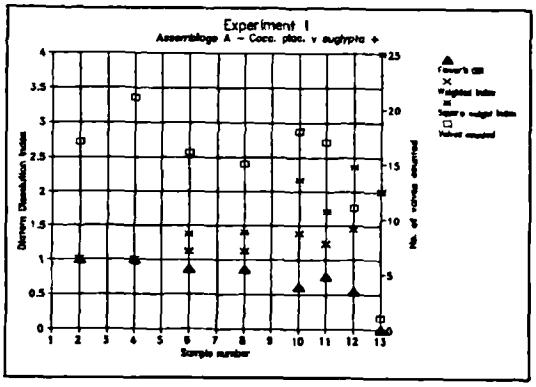
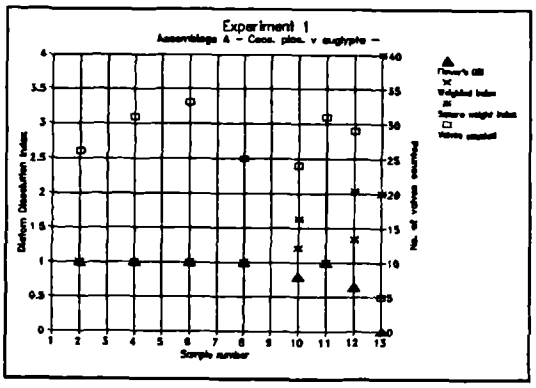
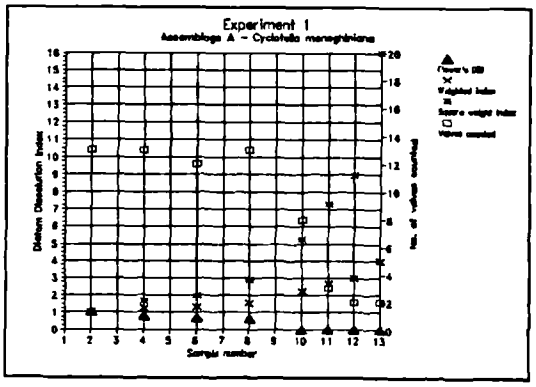

F
2503 25K

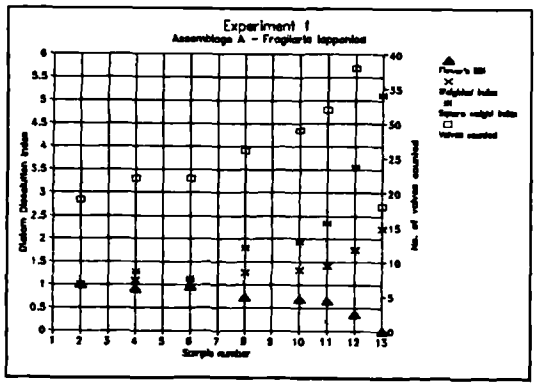

G
506143 20KV X10.0K 3.0um

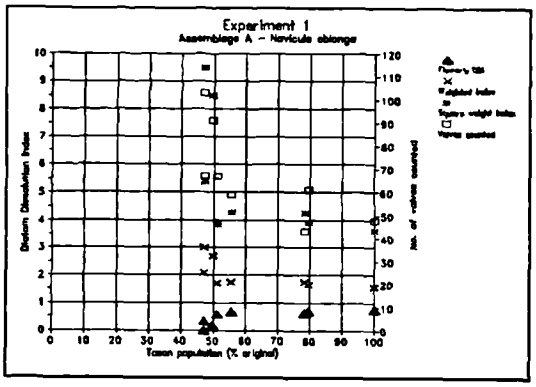


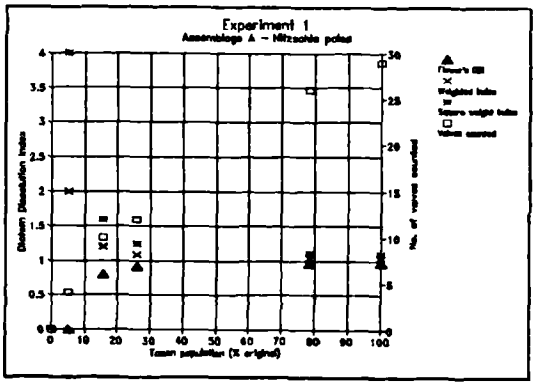


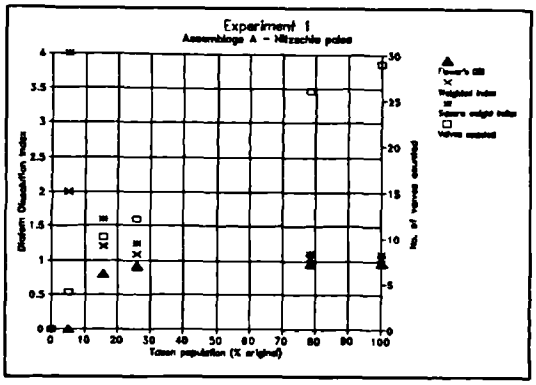




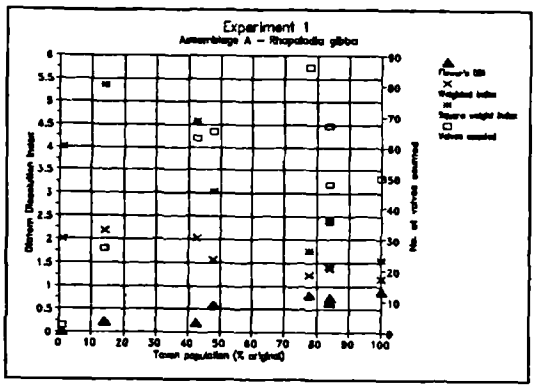


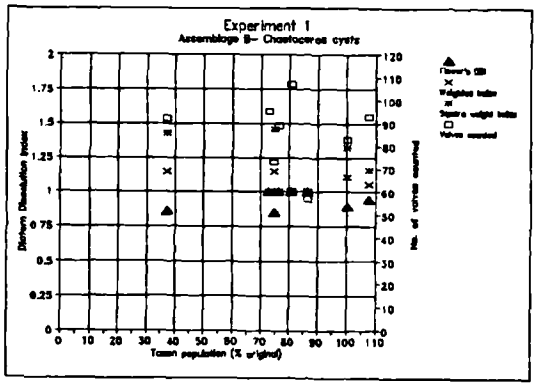


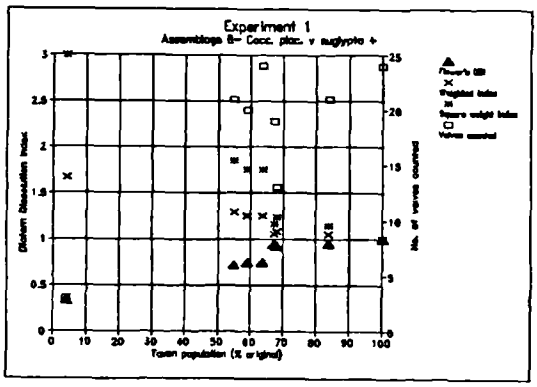


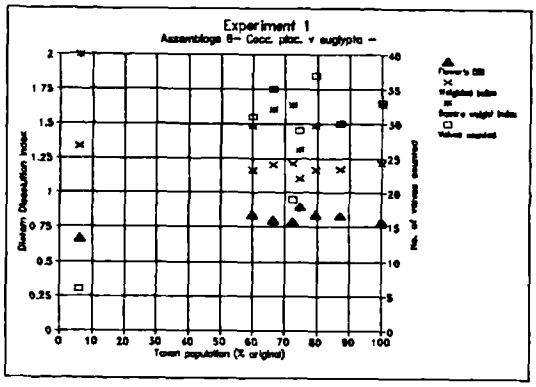


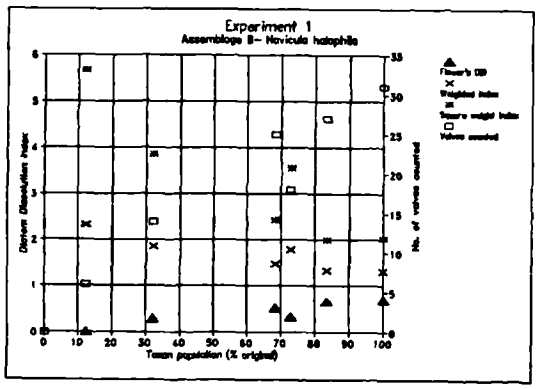
Figures A2.1-8

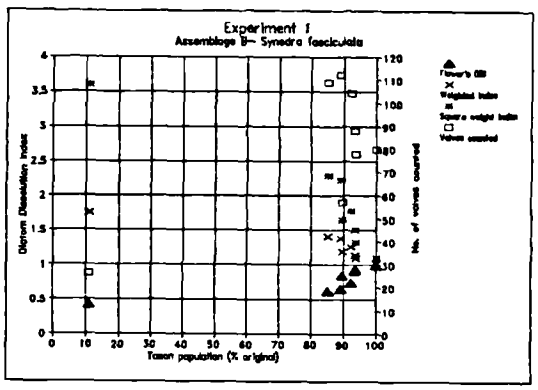


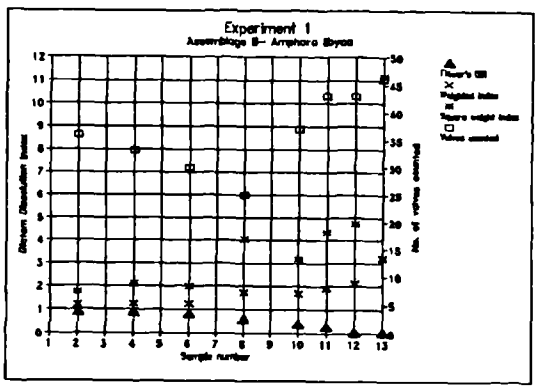


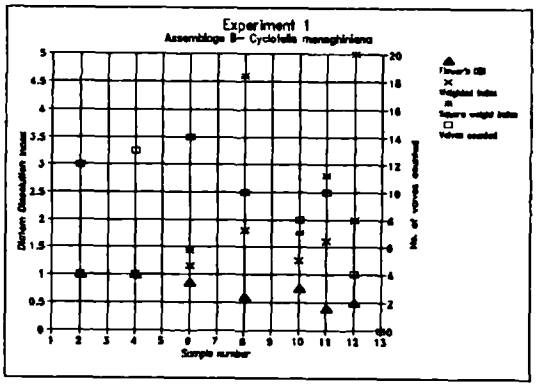




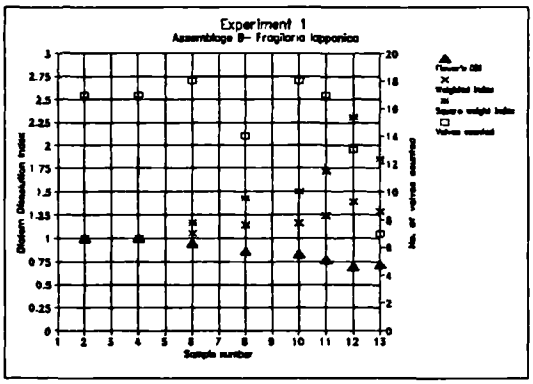


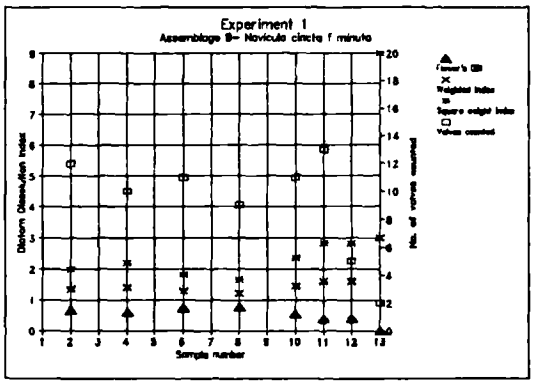


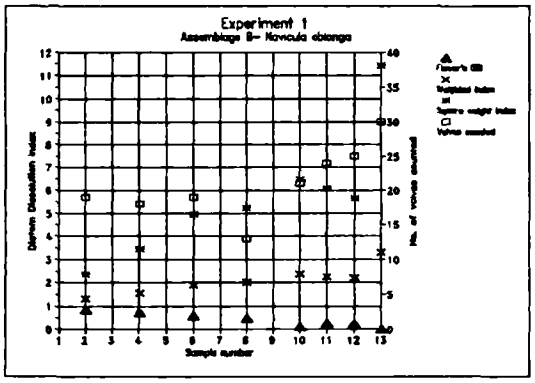


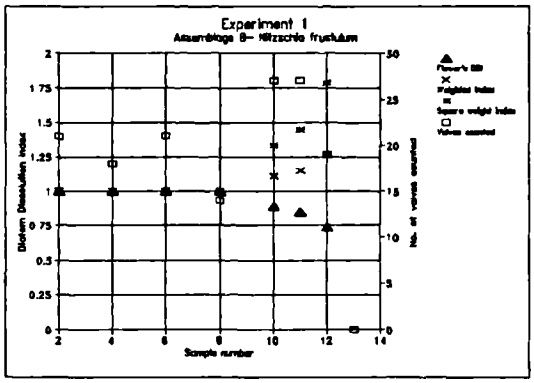


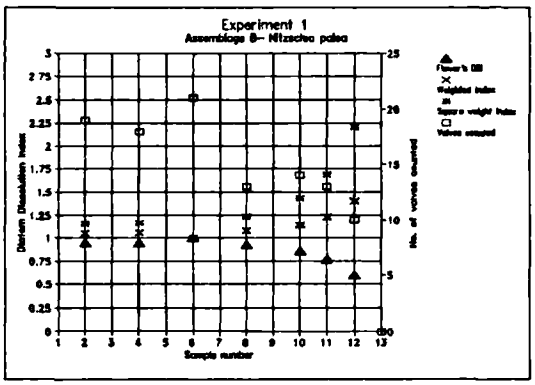
Figures A2.9-16

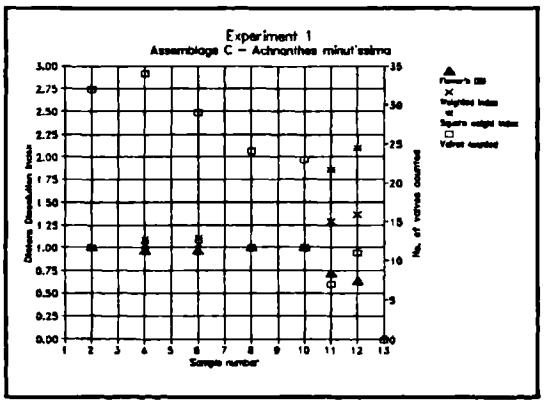


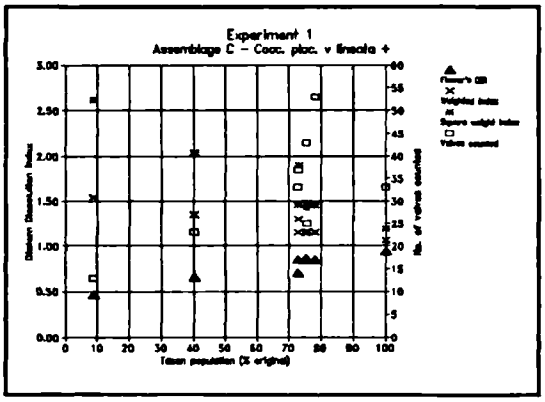


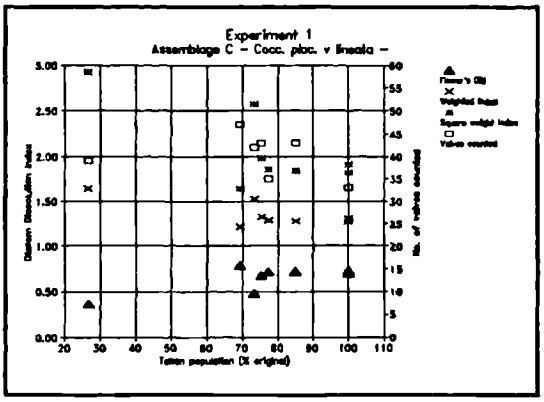




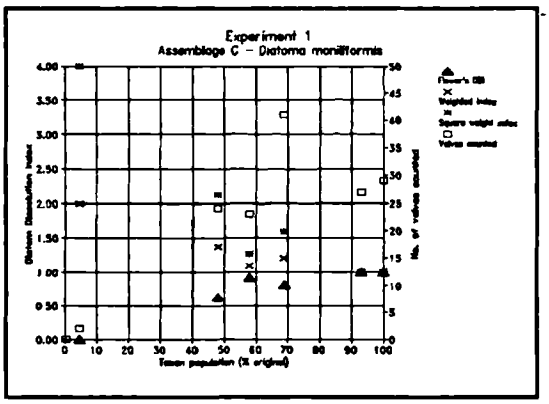


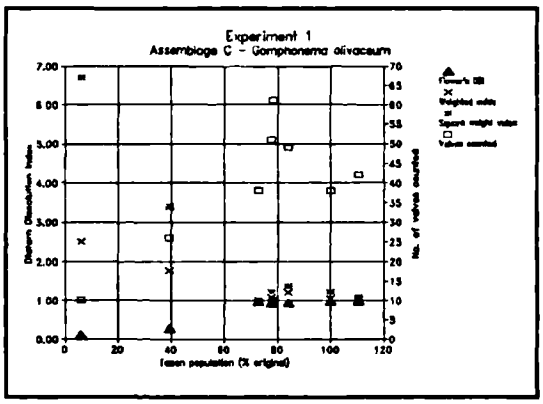


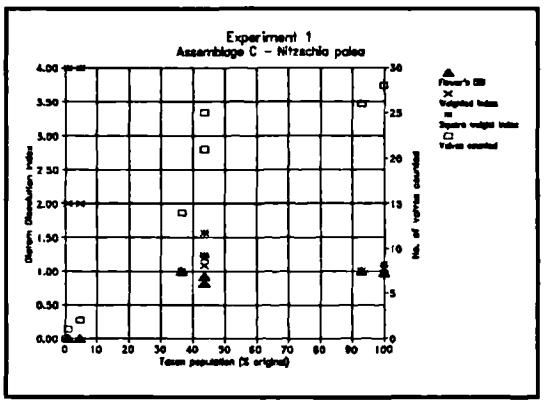


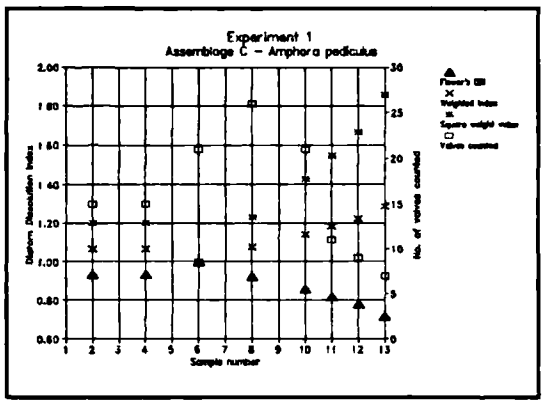


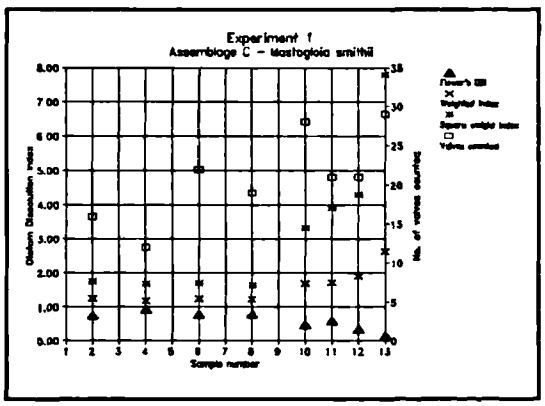
Figures A2.17-24

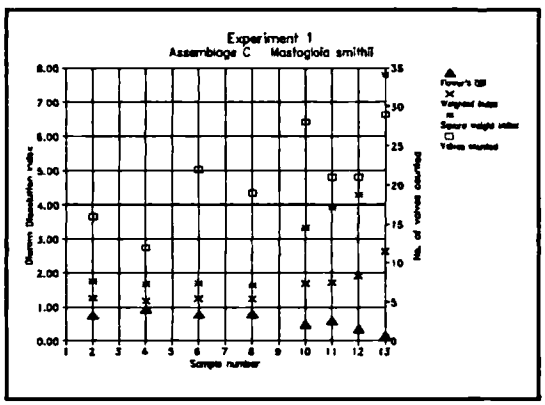


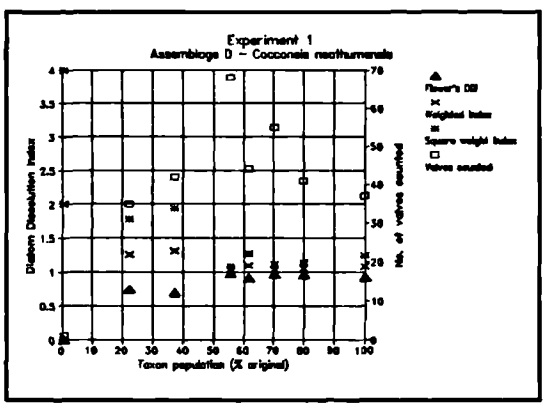


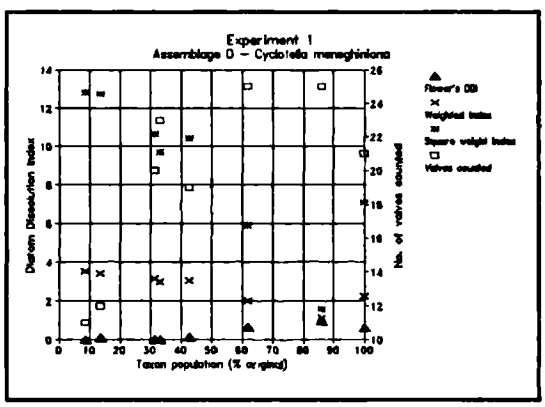












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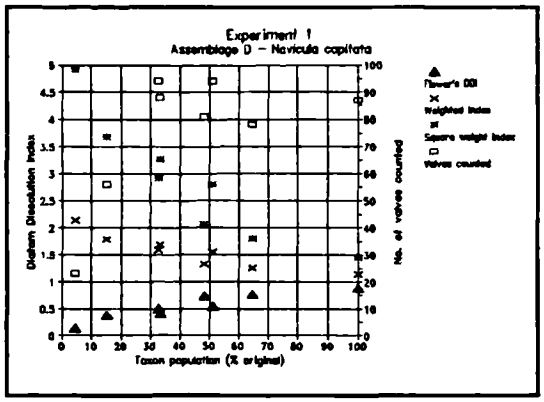

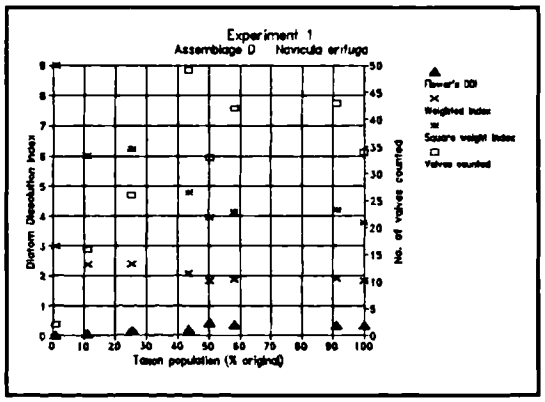

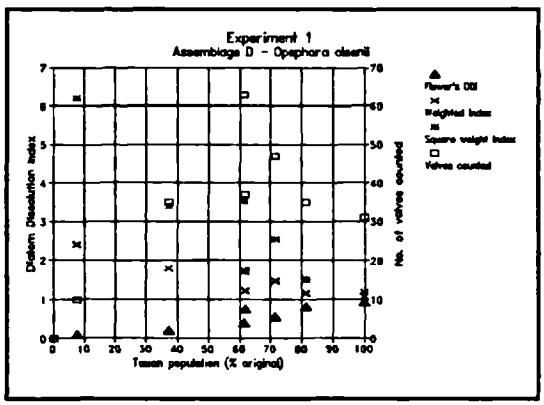

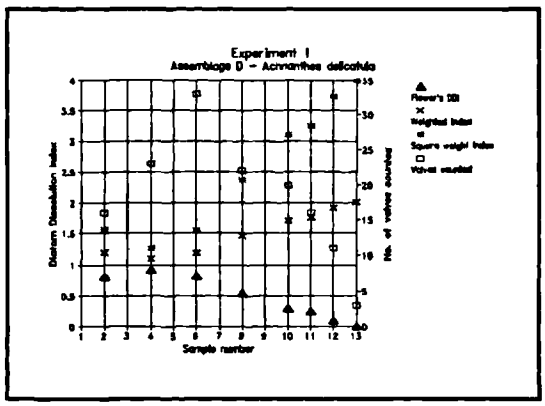

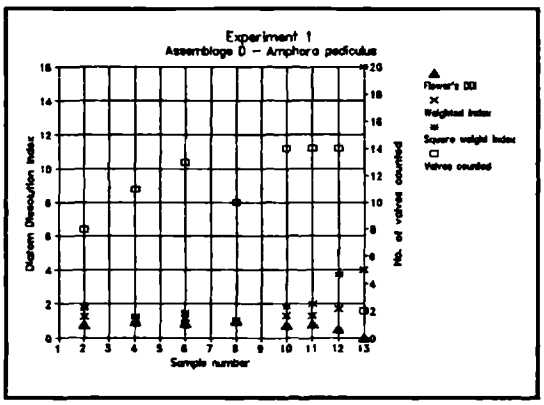

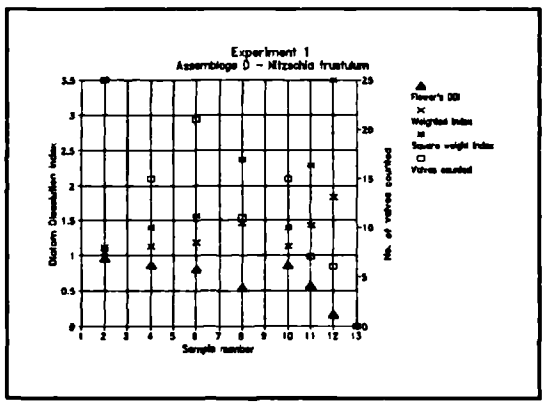

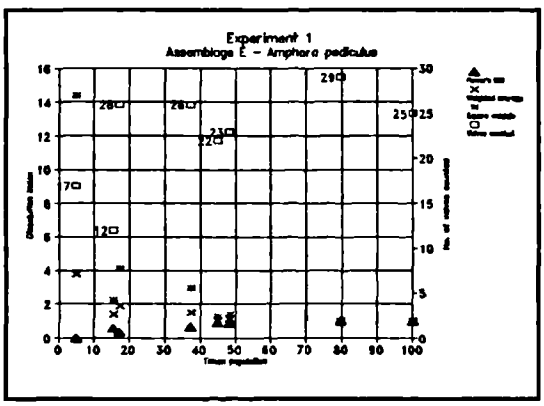

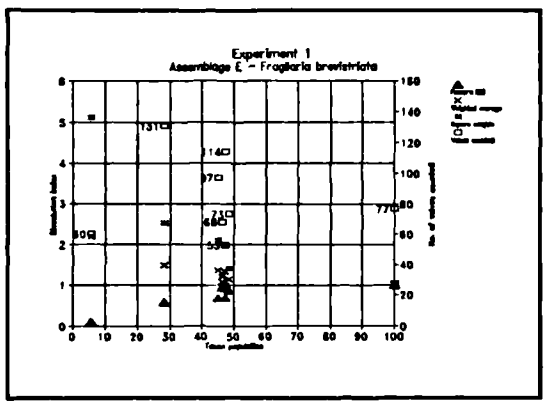

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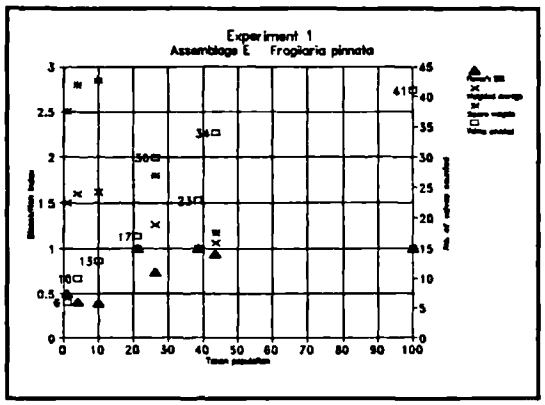

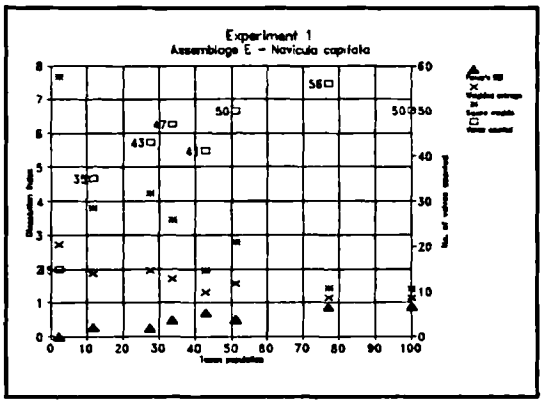

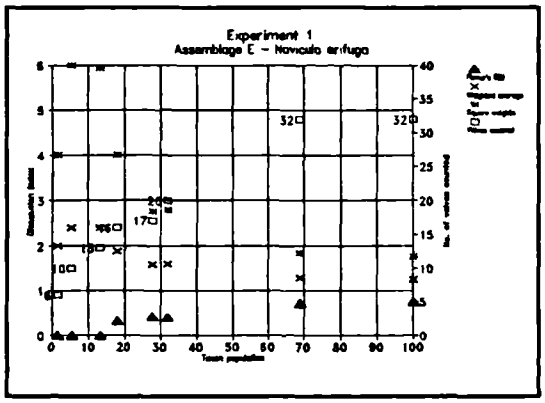

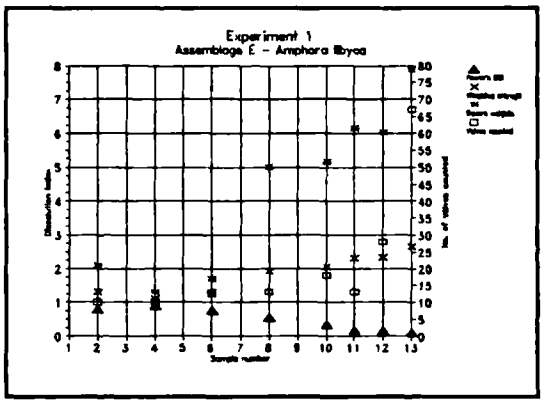

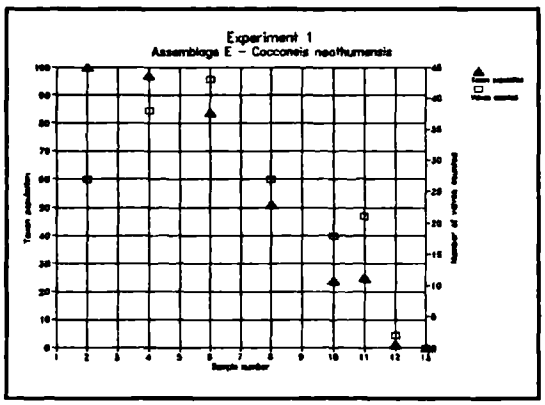

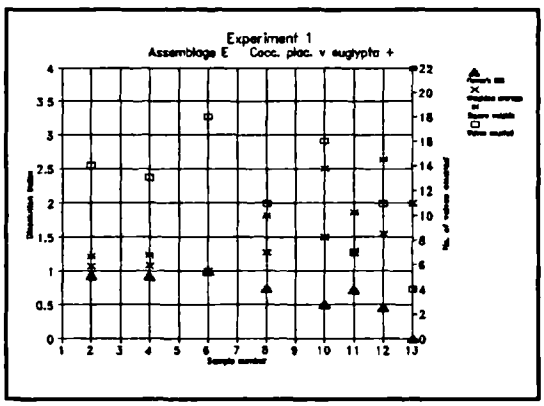

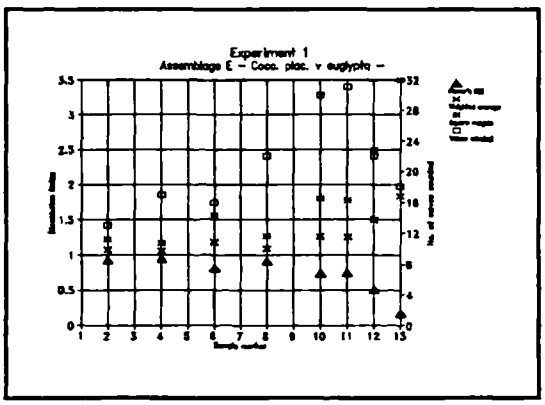

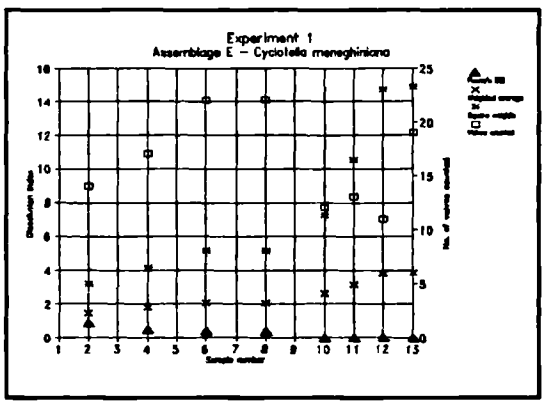

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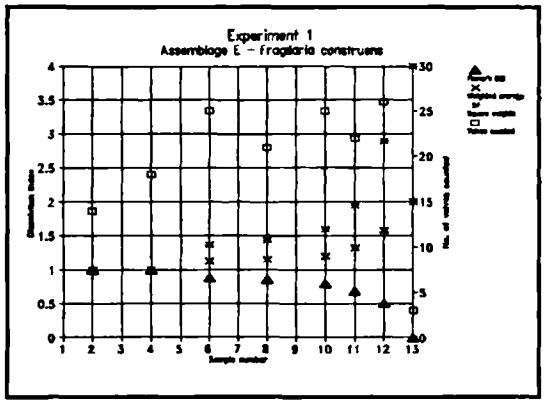

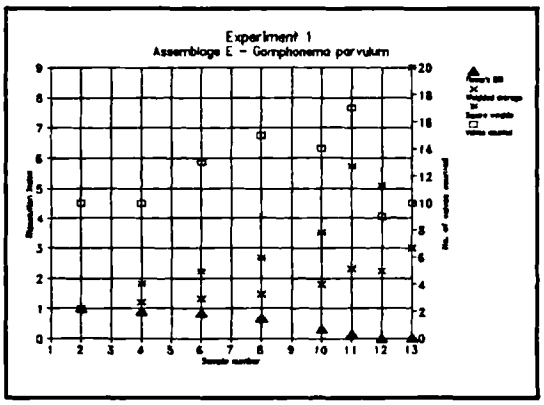

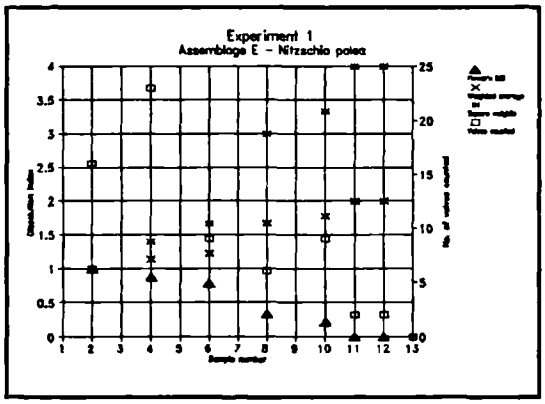

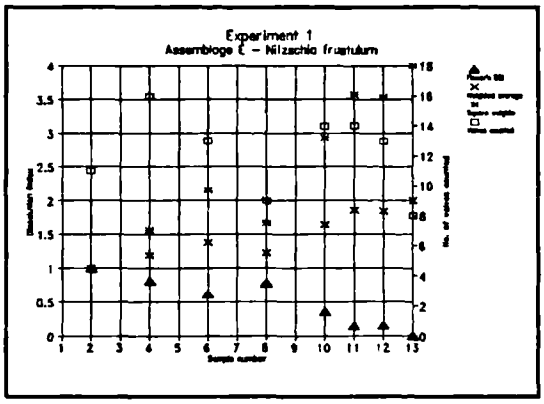

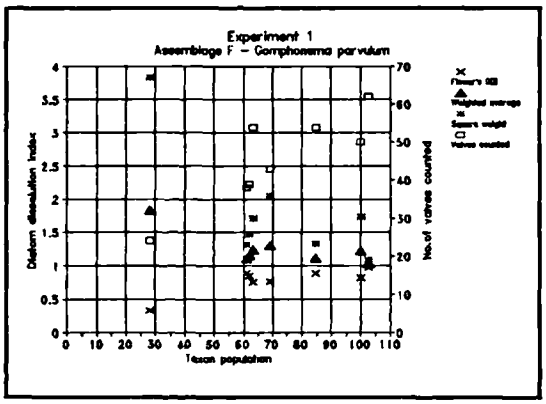

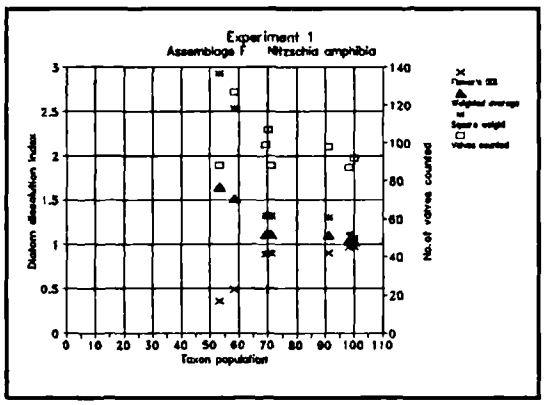

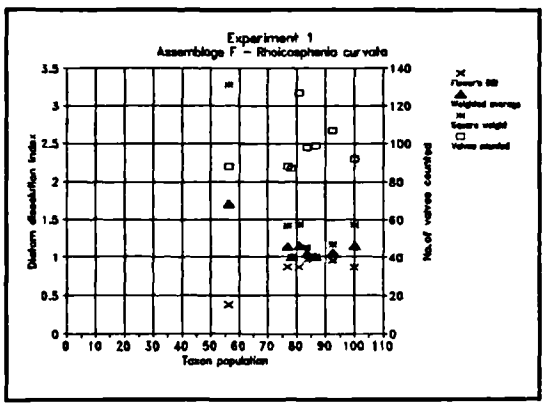

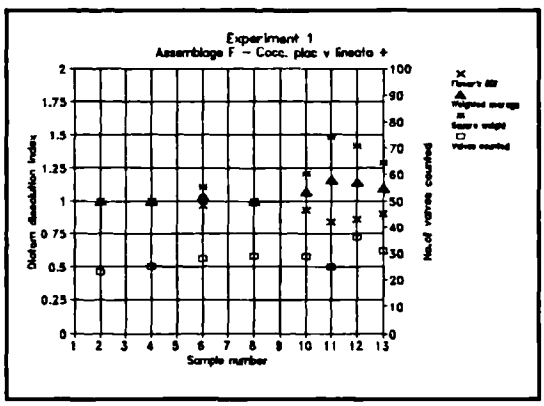

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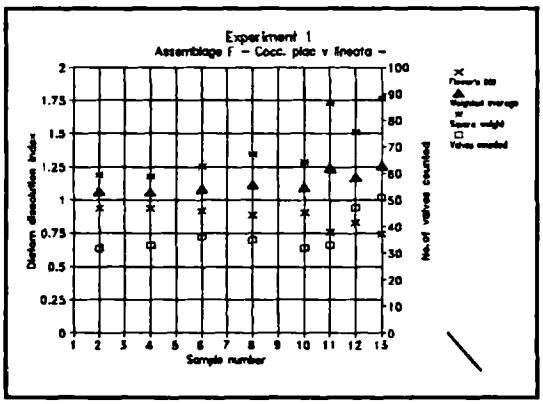

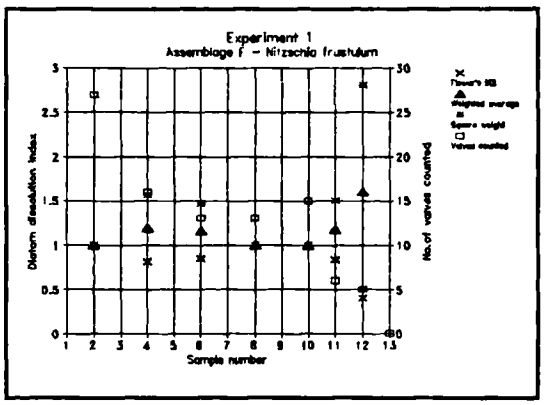

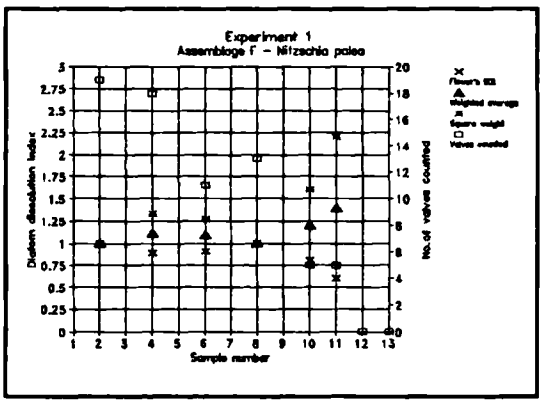

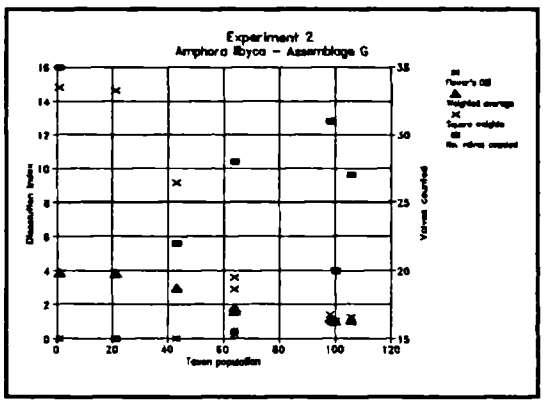

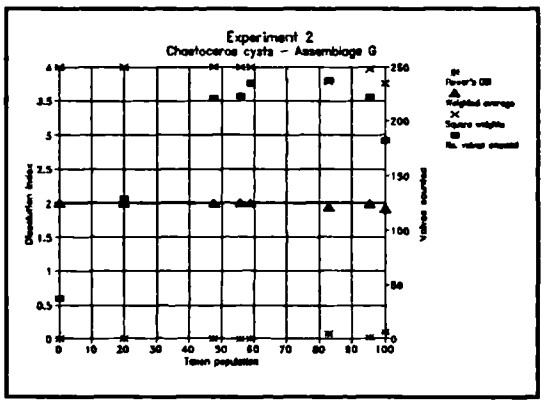

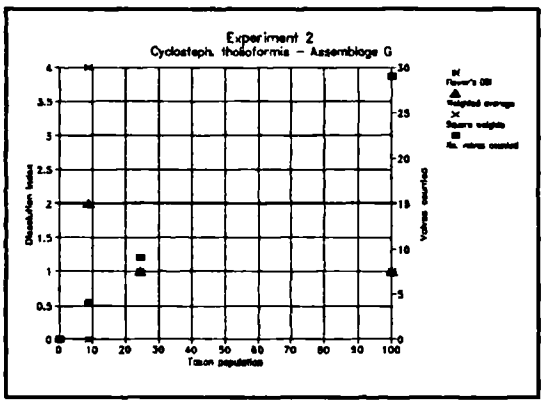

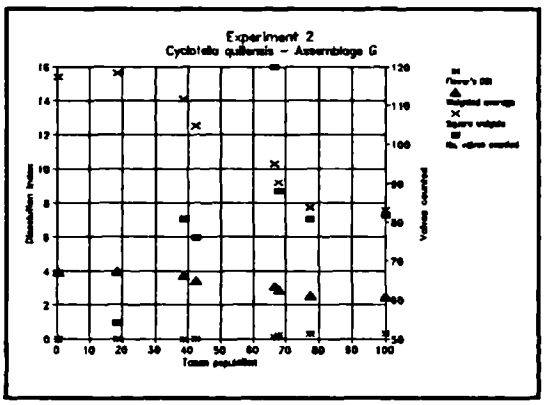

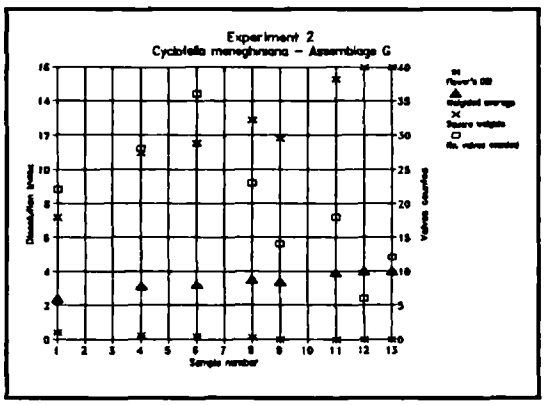

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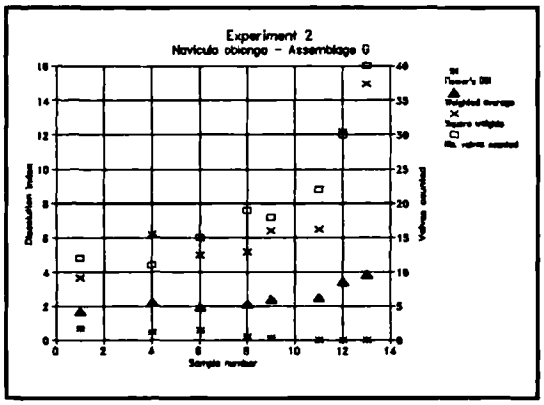

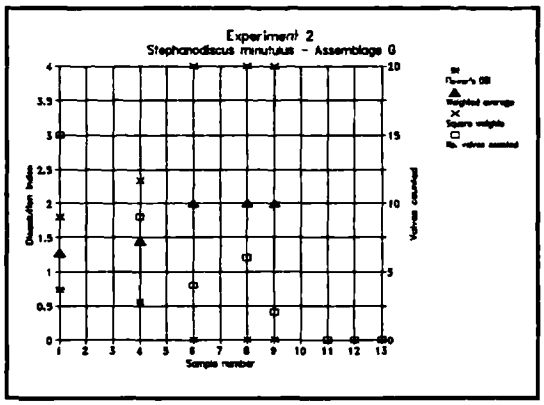

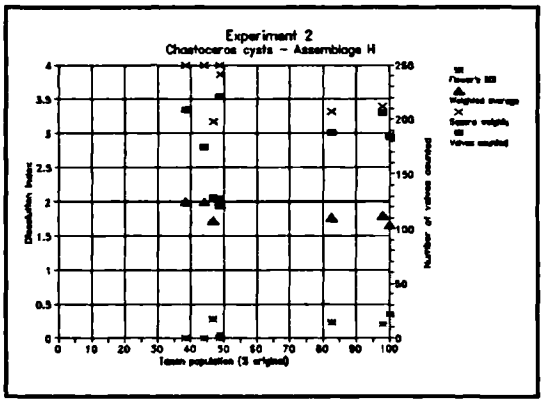

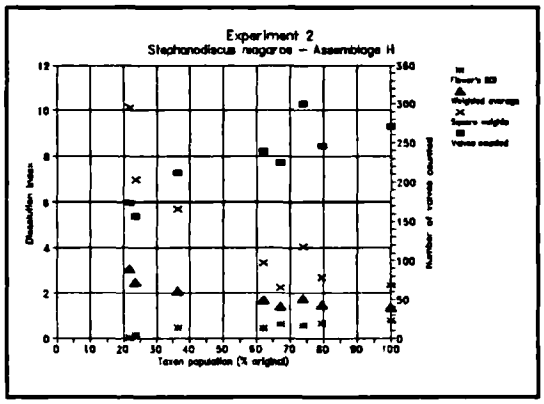

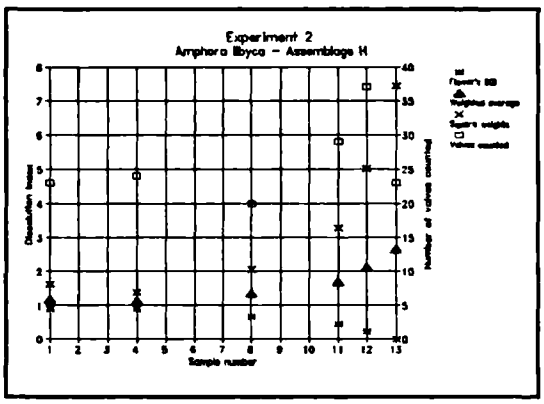

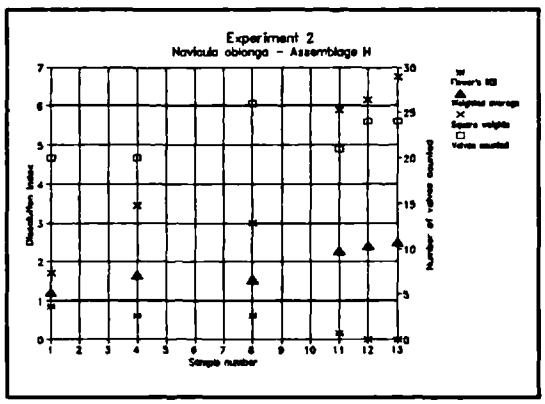

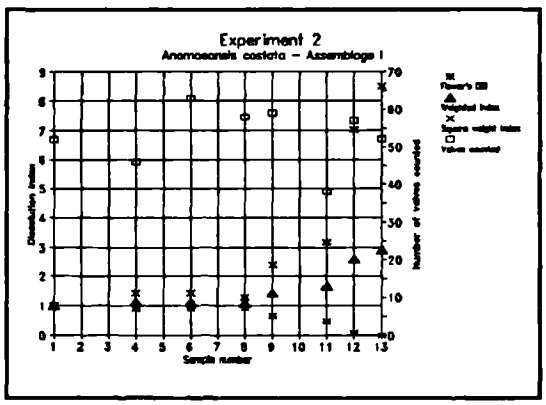

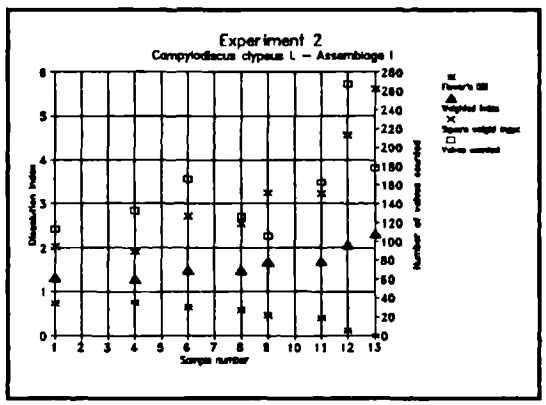

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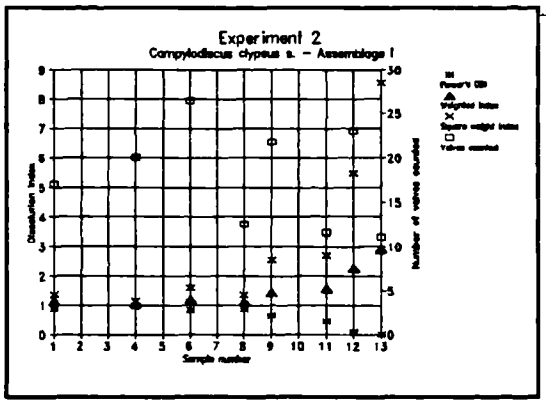

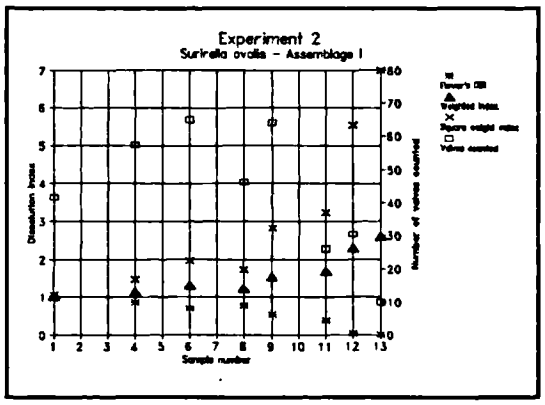

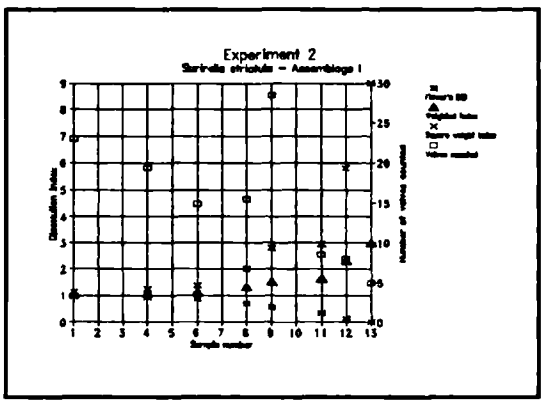

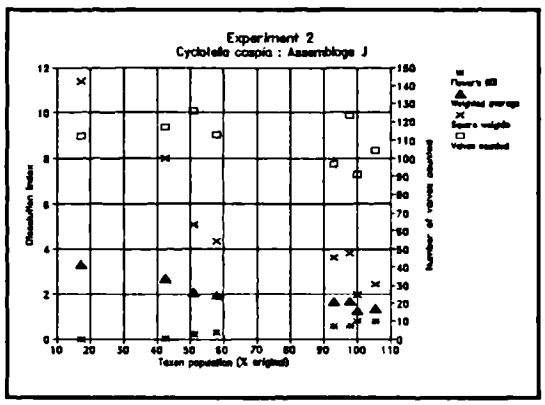

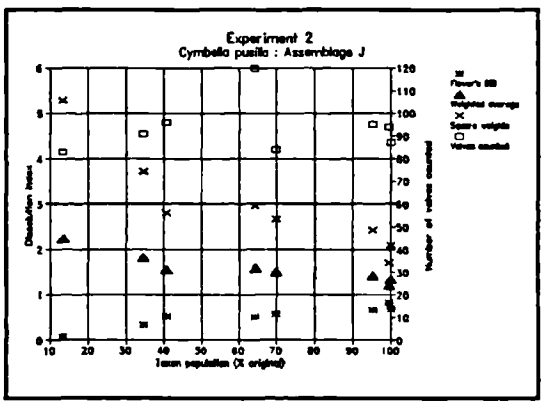

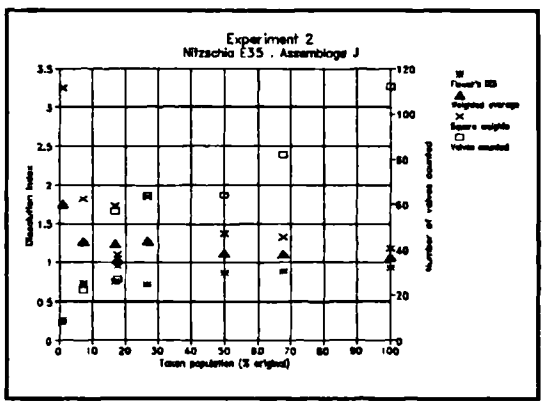

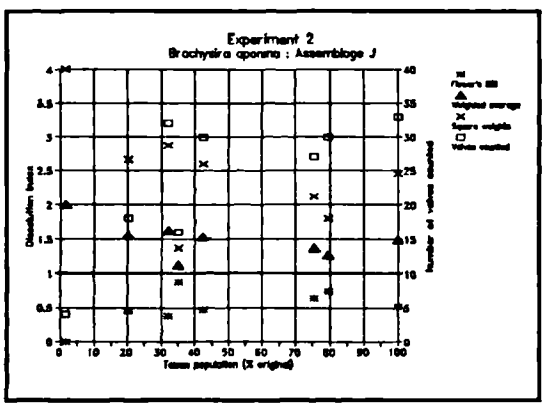

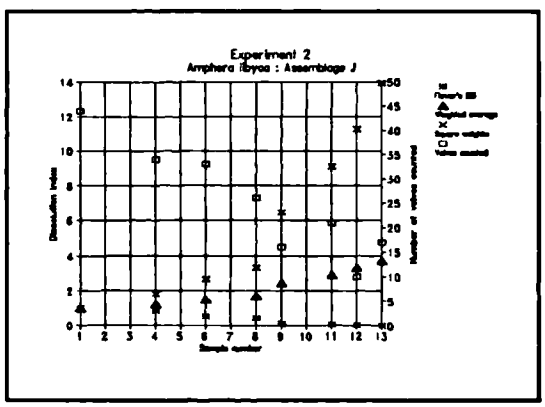

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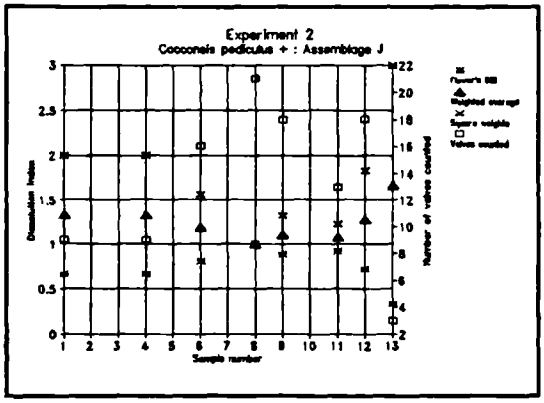

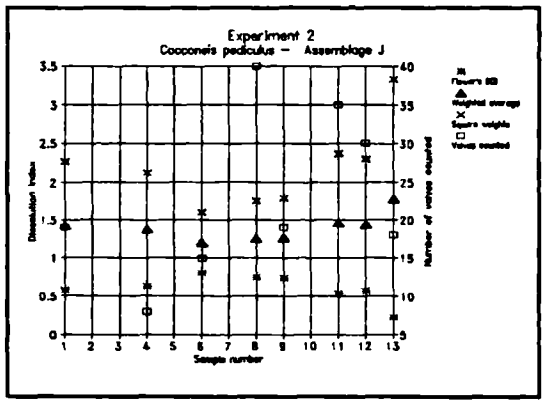

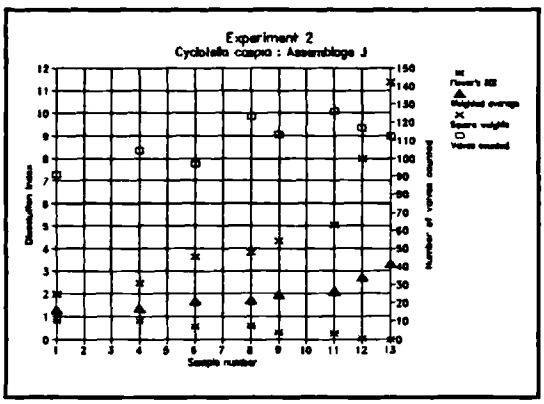

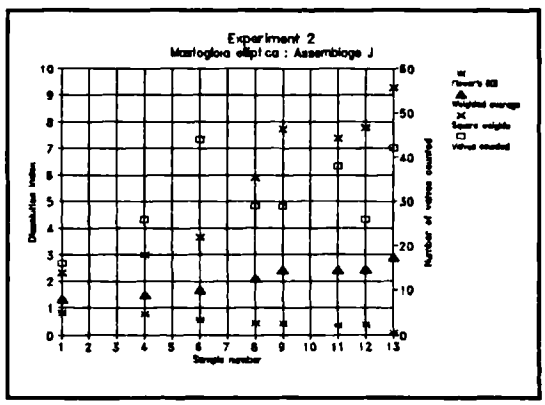

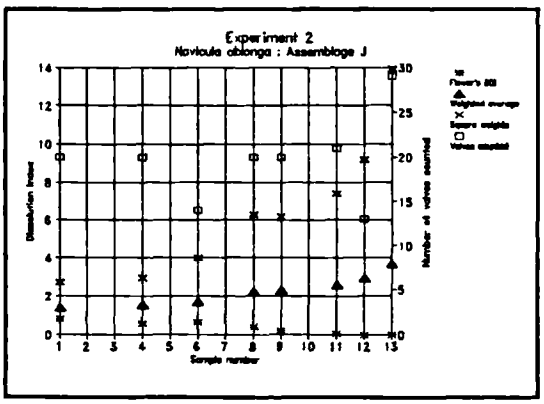

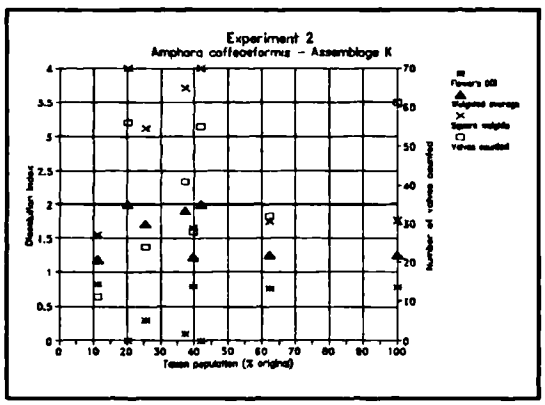

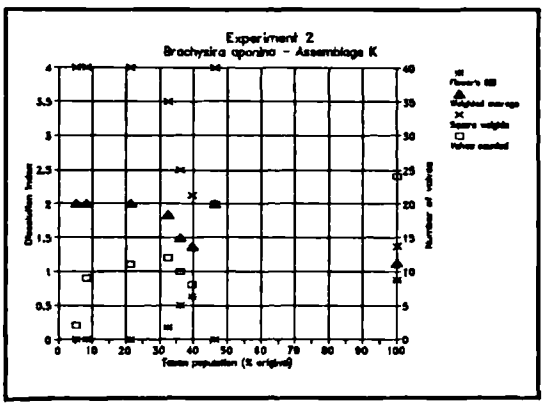

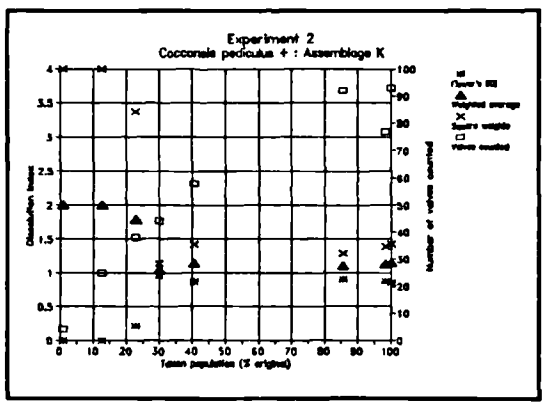

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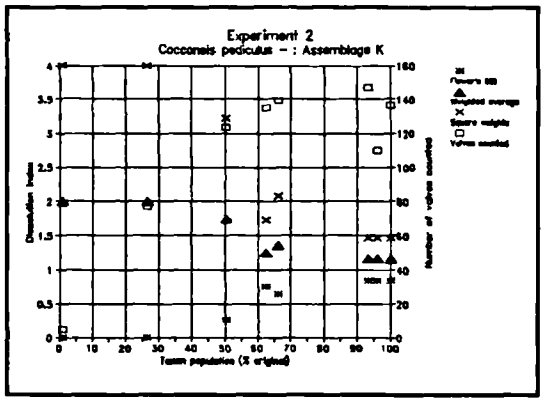

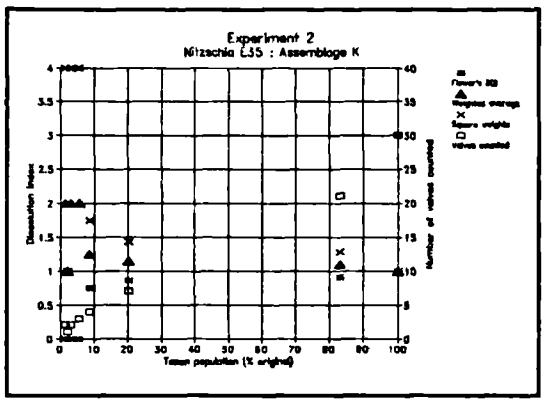

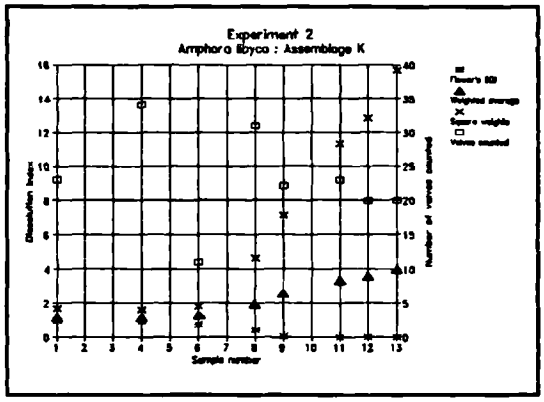

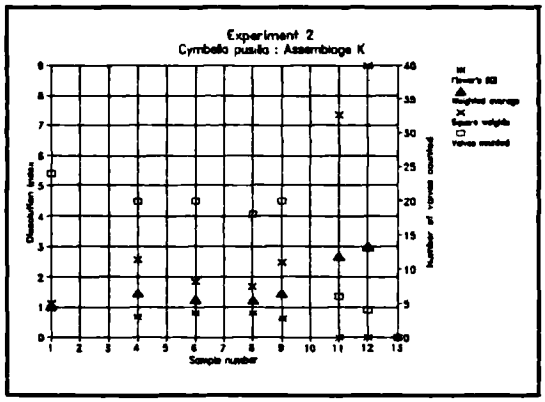

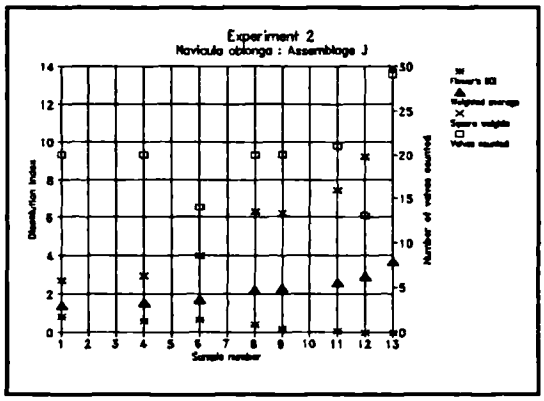

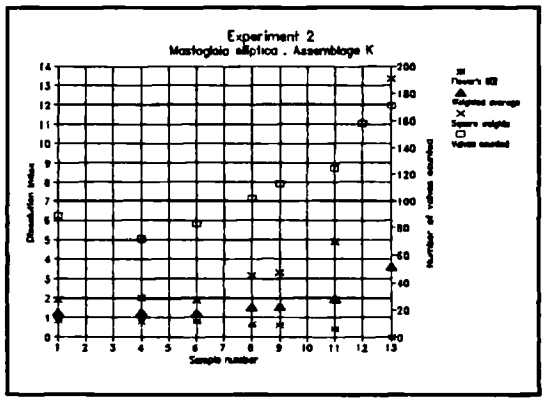

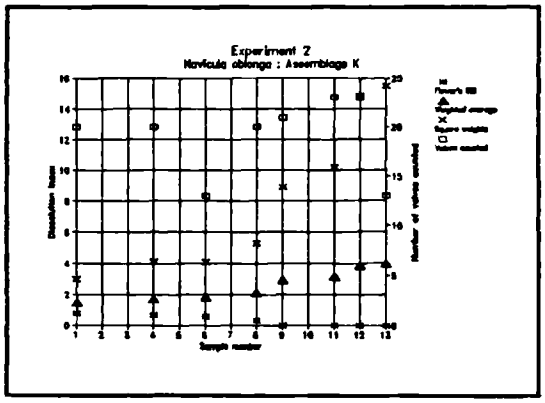

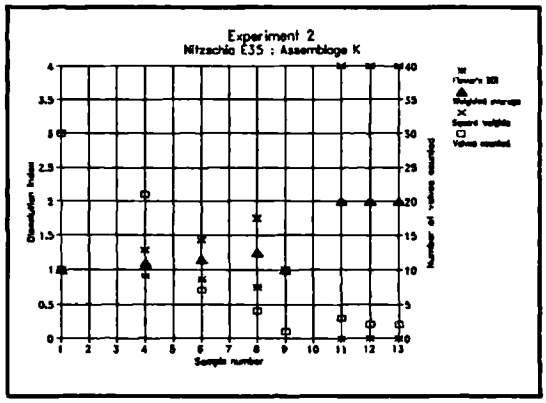

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