Deliverable 12: Management Tool

MOLTEN

Monitoring **l**ong-**t**erm trends in **e**utrophication
and **n**utrients in the coastal zone:
Creation of guidelines for the evaluation of background
conditions, anthropogenic influence and recovery

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Forward

The report was generated as part of the EU funded (EVK3-CT-2000-00031) **MOLTEN** project and should serve as technical guidelines to determine *reference conditions* in estuaries as required by the Water Framework Directive.

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ANNEX 1. The MOLTEN Diatom Database and Transfer Functions

Executive summary

Estuarine and coastal systems have experienced massive changes in nutrient loading from anthropogenic activities during the history of human occupation. Attempts to determine the long-term effects of nutrient enrichment are hampered by the limited time span of contemporary monitoring programs: Most monitoring programs began only in the last 30 years, thus severely limiting our perspective on when changes began, and what the starting point was prior to anthropogenic impact. Ultimately, these constraints limit our ability to manage and protect our aquatic resources. Without knowledge of past conditions it is difficult monitor the effectiveness of nutrient reduction policies, or even know what are appropriate restoration targets for degraded ecosystems. Given the lack of long-term chemical or biological monitoring, questions about the long-term effect of nutrient enrichment can only be answered using paleoecological methods, that is, the record of chemical and biological changes contained in well-dated sediment cores.

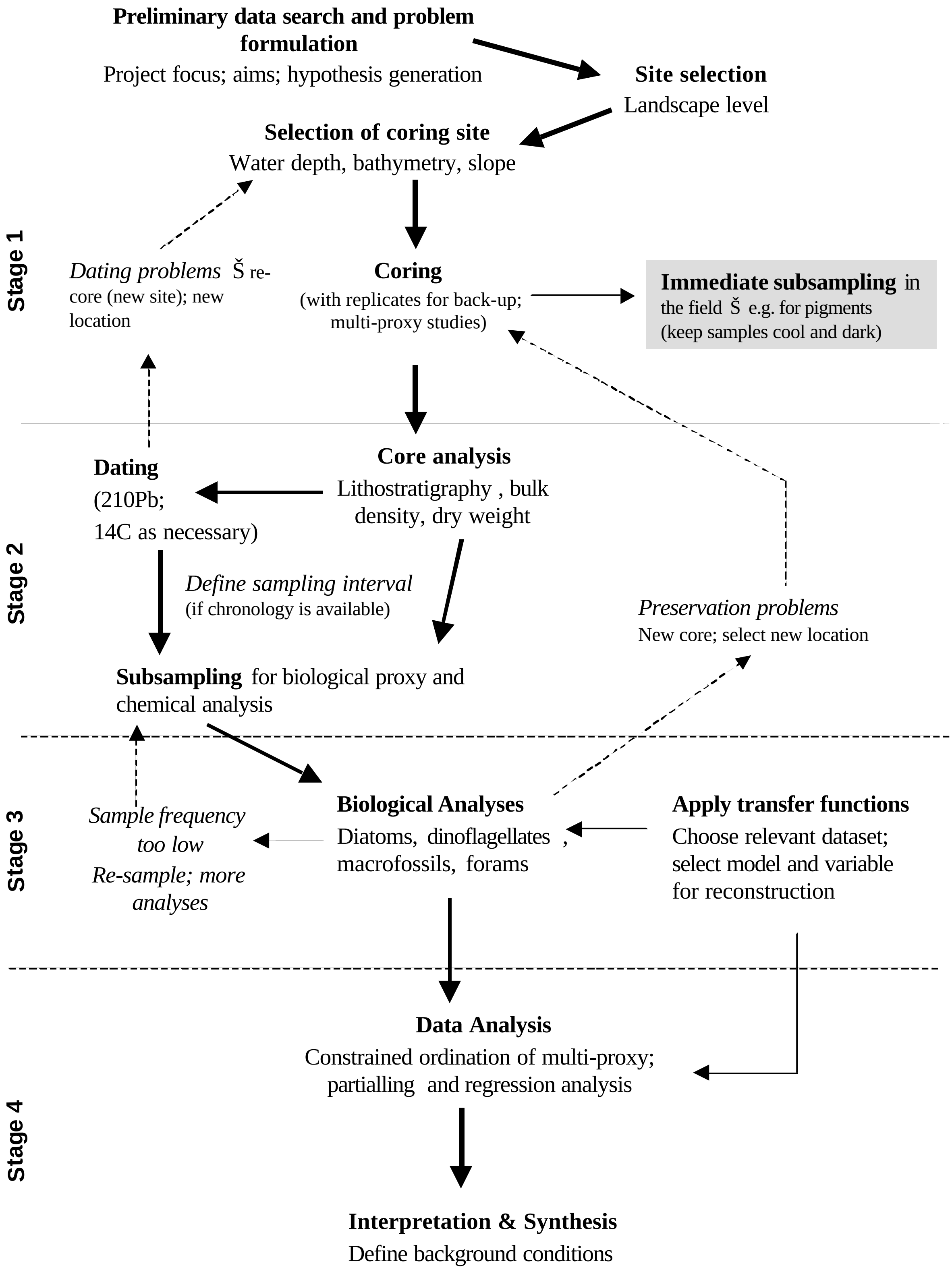
The overall objective of the EU funded **MOLTEN** Project was to develop a paleoecological methodology for environmental decision makers that can be used to assess background or *reference conditions* and the degree of past and present departure from these conditions, and to predict the likely recovery of these systems with reduced nutrient loads, such that appropriate policy and management measures can be taken both at the European and national scales.

The present “Management Tool” has been completed and is presented here. This report should serve as technical guidelines or as a “how to” guide on using paleoecological methodology to determine reference conditions in estuaries. We have used this methodology successfully in several European estuaries (Clarke et al. 2003; Weckström et al. 2004). In addition, the paleoecological approach to determining reference conditions has been applied to the Roskilde Fjord estuary (Andersen et al. 2004).

The guide starts with a flow chart that summarizes and outlines the steps needed to carry out a paleoecological study in an estuary and is followed by in-depth information regarding each step in the process. This report includes both practical details and theoretical considerations. The first section summarizes the paleoecological approach and then detailed methodologies are presented for site selection, sediment coring, dating, and the importance of other proxies in carrying out a paleoecological study. The next section is a step-by-step guide to hind-casting total nitrogen concentrations. This section includes information on taxonomic harmonization and using the **MOLTEN** database. The report ends with methods to evaluate the reconstruction of nutrient concentrations. An Appendix is attached that serves as a User Guide to the **MOLTEN** Diatom Database and Transfer Functions.

Additional information can be found on the MOLTEN web site (http://Craticula.ncl.ac.uk:8000/Molten/jsp/index.jsp).

Flow chart for an coastal palaeoecological study



1. Review of the Paleoecological Approach

What is a transfer function?

A **transfer function** defines the relationship between the inputs to a system and its outputs. In paleoecology and paleolimnology, transfer functions simply describe the relationship between organisms and their environment with the ultimate goal to to use the present-day ecology of organisms to infer past conditions. Transfer functions are established using the recent organism assemblages and measured environmental variables from a *calibration* or *reference* data set. These calibration sets involve sampling a range of sites (e.g., lakes, estuaries) for a suite of environmental variables, which are then related to the biological indicators (e.g., diatoms, ostracods) preserved in the surface sediments of the systems concerned using numerical techniques. The data collected in monitoring programs provide an ideal opportunity to construct calibration data sets.

The mathematical methods for establishing a transfer function are based on non-linear regression techniques. The most popular approaches in palaeolimnology are the weighted averaging (WA) and the weighted average partial least squares (WA-PLS) methods. After estimating environmental optima and tolerances of indicator taxa using the most appropriate modelling scheme, the transfer function is applied to organism data from a sediment core to quantitatively reconstruct the parameter values of the key environmental variable(s) affecting the distribution of the organisms in the modern reference data set. The major steps involved in the application of a transfer function are illustrated in the first figure.

Paleolimnological approaches are now being applied to a wide array of eutrophication-related problems, with many new methodologies currently being implemented. Experiences from lake environments are encouraging. Although nutrient transfer functions are not as strong as those originally developed for lakes, i.e. lakewater pH, they are sufficiently robust to infer long-term trends in the directions and magnitude of eutrophication. In a few cases where long-term monitoring data have been available, comparisons between diatom-inferred and lakewater nutrient levels have shown relatively good correspondences (e.g., Bennion et al. 1996; Lotter et al. 1998; Bradshaw and Anderson 2001). In addition to diatoms, other indicators such as chrysophyte stomatocysts, chironomids and cladocera have been used to hindcast trends in past nutrient concentrations in freshwater environments.

Application of transfer functions to coastal environments

Paleoecological studies on estuaries have much more rarely been attempted, as they typically have complex and variable sedimentation patterns in space and time, and resuspension of sediments can be a serious problem. According to the results achieved during the MOLTEN project, transfer function approaches based primarily on diatom compositional data can be used to track cultural eutrophication patterns only roughly in sites where reliable sediment deposition zones have been identified (Clarke et al., 2003; Weckström et al., 2004). These successes should certainly encourage future endeavors, but a more reliable assessment of trophic conditions would involve the usage of multi-proxy approaches.

2. Site selection

Level 1 – Study Area

A successful project requires careful evaluation of all possible sites prior to the selection of the final study site. After the definition of the project aims and problem formulation, the proposed study site should be chosen after an evaluation of all available data both in terms of previous paleoecological studies, water quality monitoring data and land-use data (historical and contemporary classifications) where relevant (i.e. restricted embayments or estuarine sites with extensive land-water interfaces). Where there is a range of monitoring and documentary information available for a given location, preference should be given to this location as these data can facilitate interpretation of the sediment core data. These requirements may have to be modified by considerations about the sedimentation environment (see below).

Level 2 – Core Location

After the location (fjord, embayment) has been selected, possible coring sites should be identified on the basis of available bathymetric charts. It is generally advisable to core in the deepest part of the basin as sediment accumulation rates are often highest there, wind-induced resuspension will be minimalized and seasonal anoxia (if the basin is deep enough to stratify) can reduce bioturbation by benthic invertebrates. Both resuspension and bioturbation can cause substantial problems for ^{210}Pb dating (see below). The benefits of using a deep-water site can substantially outweigh problems associated with core representativity.

3. Sediment coring

There are a variety of sediment coring devices available for use in shallow coastal waters, most of which were developed for lakes. Most of these corers (e.g. Haps corer, Kajak, etc.) will readily recover sufficient sediment for the majority of projects that are undertaken as part of a contemporary water quality management program. The use of wide diameter corers is advisable wherever possible (to increase the size of the available sample). There are, however, sites where sediment accumulation rates are so high (> 2 cm/yr) that a 1-m sediment core will not reach pre-disturbance conditions (i.e. pre-20th century). Unfortunately, this is generally not known until preliminary dating is completed, hence the importance of checking for previous studies and available data. In these situations alternative techniques will be required (e.g. large Kullenberg corers), many of which will destroy (blow away) the uppermost, more flocculent layer of sediment during penetration. In these situations a surface core that overlaps with the underlying core is required; this can often be correlated by means of carbon profiles.

It is vitally important that the uppermost sediment layer are retrieved, both to provide a sediment record that covers the whole time span of interest (i.e. up to the present) but also because its loss can lead to errors in the ^{210}Pb chronology (due to an incomplete ^{210}Pb inventory – see below).

After retrieval, cores should be stored in an upright fashion (where appropriate), kept cool (ca. 4°C) and in the dark. Cores should be sectioned and sub-sampled as soon as possible.

Sub-sampling and basic sediment analyses

It is standard practice to section sediment cores at 1-cm intervals, although as the chronology is rarely known in advance (unless the site is being re-visited) this can prove to be either too coarse or too fine, depending on the sediment accumulation rate.

If HPLC pigment analysis is to be undertaken as part of the study special care should be taken with the core sections. In some instances sectioning in a low O_2 conditions is advisable. Any subsample of an individual core slice that is to be used for pigments should be immediately placed in the dark and then frozen as soon as possible.

After the core has been sub-sectioned, the individual core slices should be divided into three subsamples for :

1. lithostratigraphic analysis,
2. micro- and macrofossil analysis
3. dating.

Basic parameters such as bulk density (percentage dry weight) and loss-on-ignition at 550°C (or carbon and nitrogen content via an elemental analyzer) are important and should be undertaken on every sample. (The use of an element analyzer is the optimal approach as the required sample size is smaller than that for LOI). These data can be important for core correlation, both of a long core to a surface core, of replicate cores or of a more marginal core taken for macrofossils to a central, dated core.

The sediment section for dating should then be dried (preferably freeze-dried) while the sub-samples for fossil analysis should be kept cool and dark or frozen. ^{210}Pb (by gamma counting) is non-destructive and so some analyses can be undertaken on this sediment sample after dating analyses are complete. If possible a small sub-sample from each level should be retained for archive use or re-analysis.

4. Dating

Dating forms an integral part of any paleoecological study. Although a variety of techniques can be used (e.g. pollen, carbonaceous particles – see below) the most widely used tool to date recent sediments (i.e. the last ~100-150 years) is ^{210}Pb. ^{210}Pb is a naturally occurring radioisotope from the ^{238}U decay chain with a half-life of 22.26 years. This effectively means that it can, under optimal conditions date sediments up to 150 years old, although beyond 100 years the error associated with a given age is often substantial.

Determination of ^{210}Pb by gamma counting also provides data on ^{137}Cs, ^{241}Am (both bomb-derived radionuclides) and ^{226}Ra. The latter is important as it provides a means of estimating the supported and unsupported components of the ^{210}Pb – the chronology being derived from the unsupported fraction. In the absence of ^{226}Ra the unsupported component is estimated by subtracting the supported ^{210}Pb concentration, which is estimated as the mean concentration of ^{210}Pb after its concentration stabilizes below a given depth. This approach is problematical as the concentration of ^{210}Pb/^{226}Ra may not be constant.

It is important to realize that ^{210}Pb chronologies are dependent on the dating model that is chosen. The underlying assumptions can result in large differences in the final chronology. Where the ^{210}Pb distribution in the sediment is optimal (a log-linear decline with increasing sediment depth) the models will give essentially the same result.

Warning: Where the ^{210}Pb distribution is non-uniform, as in many estuarine and near-coastal environments, the choice of model/approach is critical. In these situations, supplementary information from other dating methods is extremely useful. The main causes of non-uniform distributions are sediment mixing and variable sediment accumulation rates.

^{210}Pb is normally undertaken by specialist agencies/consultancies which will provide help with deriving the ^{210}Pb chronology.

Problems with ^{210}Pb and dating estuarine and coastal marine sediments
The primary problem with the dating of estuarine and coastal marine sediments is that the energy input to the system (as wind, currents and tides) is considerably greater than that to lakes, with the result that resuspension of sediments is considerable. Resuspension results in non-uniform sediment distribution, erosion and mixing of the uppermost, unconsolidated sediments. The former can create hiatuses while the latter temporally smooths and destroys the resolution of the microfossl record as well as affecting the ^{210}Pb distribution.

Mixing by resuspension or benthic invertebrates is a major problem affecting ^{210}Pb in marine environments, but a secondary problem is that of non-uniform ^{210}Pb distribution due to variable sediment accumulation rates. With the substantial land-cover changes that have affected coastal margins and estuarine catchments, sediment inputs to coastal marine embayments have increased substantially. The constant rate of supply (CRS) model, developed for lakes (Appleby 2001), is relevant in these circumstances but has not been widely adopted by marine sedimentologists.

Warning: dating is critical for the success of the project and given the problems associated with ^{210}Pb chronologies from cores derived from suboptimal locations, considerable effort should be spent on carefully selecting coring sites, both at the regional and within-basin scales.

Other dating techniques
There are a variety of other techniques that can be used to supplement ^{210}Pb dating of recent sediments. Most relevant is ^{137}Cs, which can be important in providing independent corroboration of the ^{210}Pb chronology. Spheroidal carbonaceous particles (SCPs), produced by oil and coal combustion can also be useful although, as with ^{137}Cs, they only provide a selected number of dates (for unambiguous features in the profile). Pollen can provide dates for selected horizons, e.g. the introduction of exotic plants and extensive conifer plantations in estuarine catchments. Where sedimentation rates are very low it may be useful to obtain ^{14}C dates for selected horizons beyond the range of ^{210}Pb. AMS dates are best undertaken on terrestrial macrofossils, where available, to counter problems associated with marine reservoir effects.

5. Importance of other proxies

In order to achieve a more reliable picture of changes in past nutrient status and “ecological reference conditions” of estuarine environments, the management tool recommended by MOLTEN should include a holistic approach where multiple proxies in addition to diatoms should be analyzed from the coastal sediment (Kauppila et al., submitted). Only by combining analyses of estuarine biology (diatoms, macrofossils, ostracods etc.), sedimentation rates, biogenic silica, geochemistry, and fossil pigments it is possible to more convincingly examine the changes in water quality affecting the estuaries. There exists a variety of physical and chemical techniques that can be used to track the changes in trophic status. For example, variations in sediment accumulation rate, organic/minerogenic content, grain size, sediment thickness, and geochemical and magnetic properties preserved in sediment matrix reflect changes in trophic status and biological production. Factors such as erosion rate, river transportation, and internal sediment cycling are also reflected in the sediment composition. Sediments thus provide continuous records of internal and external changes, including rapid perturbations induced by humans.

According to our experiences in MOLTEN, the following proxy sources in addition to diatom-based transfer models are the most useful archives in yielding information of past nutrient levels in estuarine conditions:

Organic phosphorus (OP) as a rough measure of organic production in an estuary. The total concentrations of sedimentary nutrient such as phosphorus and nitrogen are of little value, as their concentrations are partially controlled by variations both in iron content and redox conditions. Also, under anoxic conditions, post-depositional mobility of these nutrient is a problem. OP is a better indicator of eutrophication, because it is less mobile and decomposes more slowly than TP.

Biogenic silica (BSi) can be used as an index of the siliceous microfossil abundance in sediments, which in most environments is primarily the diatoms. Therefore, BSi is extensively used as a proxy of diatom production and is also used to reconstruct changes in paleoproductivity.

Stable isotope of d^{15}**N** serves as a specific tracer of eutrophication in nearshore environments. There is often a good correlation between δ^{15}N and other eutrophication indicators (diatom infered total nitrogen, organic phosphorus, sedimentary pigments) in the sediments cores.

Sedimentary pigments. The concentration of chlorophyll *a*, including its degradation products, indicates total algal abundance and can be used as a rough measure of productivity.

6. Hindcasting total nitrogen (TN) concentrations using the MOLTEN diatom-based transfer functions (a step-by-step guide)

Background

This section gives a step-by-step guide to hindcasting TN concentrations from sediment-core diatom assemblages using the MOLTEN transfer functions.

The transfer function approach to hindcasting is a 3 step process. Firstly, the taxonomy of the sediment core diatom counts must be harmonized with that of the training set. Secondly, an appropriate transfer function is chosen and applied to the fossil diatom assemblages. Finally, the results of the hindcasting procedure must be carefully evaluated to assess the reliability of the nutrient reconstructions. A user guide that gives details on the practical application of the MOLTEN transfer functions is also available from the MOLTEN website. A review of the transfer function approach to hindcasting can be found in Birks (1995).

Taxonomic harmonization

The MOLTEN transfer functions model the relationships between the distribution and abundance of diatom taxa and the nutrient concentration of overlying waters. These models are generated using a training set of modern surface sediment samples and associated water chemistry data. Given these relationships, expressed as a series of model coefficients, the transfer function can be applied to sediment core assemblages to predict the TN concentration under which the fossil assemblage was deposited. Since the transfer functions rely on taxon-specific responses, it is crucial that exactly the same diatom nomenclature and identification criteria are used for both the modern training set and fossil diatom counts.

In practice the matching of training set and sediment core taxonomy is achieved by using the same taxon codes in both datasets. A complete list of MOLTEN diatom taxa and their codes is listed in the user guide and on the MOLTEN web site. The MOLTEN website also contains taxonomic and distributional information for all MOLTEN diatom taxa together with images to help with the correct identification of problematic species. Once harmonized and coded in this way the taxonomy of a sediment core dataset can be verified using the MOLTEN transfer function software. This procedure compares species codes and abundances between sediment core and training datasets and reports any discrepancies.

The MOLTEN diatom-based transfer functions

The transfer function approach is based on the implicit assumption that the modern training sets encapsulate the range of chemical and other environmental conditions likely to be represented by the sediment core material. To fulfil this need the MOLTEN training sets have been chosen to cover a range of coastal environments and span the TN gradient from c. 250 to over 3000 $\mu g\ l^{-1}$. Statistical analysis of the training sets indicate that there are essentially two separate groups of samples showing regionally distinct species/environment relationships: a Western Baltic group comprising samples from Denmark and western Sweden and an Eastern Baltic group comprising samples from Finland and eastern Sweden. To this end we have merged the original MOLTEN regional datasets into the new Western and Eastern Baltic training sets and derived transfer functions for these training sets using the numerical technique of weighted-averaging partial least squares (WAPLS: ter Braak and Juggins, 1993). Analysis also indicates that these new transfer functions perform better that original regional or a single Baltic combined transfer function. We therefore recommend that the Western Baltic training set be applied to cores collected from the Western Baltic and visa versa.

Once the core data taxonomy has been coded in accordance with the training sets the transfer function can be applied using MOLTEN software. The output will be a reconstructed TN concentrations for each core sample, sample-specific prediction errors, and diagnostic statistics to aid in the evaluation of the reconstruction.

7. Evaluation of the reconstruction

All MOLTEN transfer functions will provide a quantitative TN reconstruction. An important part of the transfer function approach to hindcasting TN concentrations is a thorough evaluation of the reliability of the reconstructed values. This can be done in three ways:

1. Closest analogue analysis

Implicit in the transfer function approach is that the training set samples provide good analogues for the sediment diatom assemblages. This assumption can be tested first using the verification function described above to highlight fossil samples that contain significant numbers of taxa that are absent from the training set. A second more quantitative assessment can also be made using the MOLTEN software to find the closest modern analogues for each fossil sample based on the modern analogue technique (MAT: Birks 1995). MAT quantifies the dissimilarity between modern and fossil samples using squared chi-square distance. Analysis of the distribution of dissimilarities in the training set suggests that any fossil sample with dissimilarity of greater than 70 has no close analogues in the training set and reconstructions for such samples should be treated with caution (see Juggins and Jones 1995 for a discussion).

2. Compare reconstructions using different training sets / transfer functions

In addition to the Western and Eastern Baltic WAPLS transfer functions we also provide WAPLS and locally weighted weighted averaging (LWWA) transfer functions developed using the total combined Baltic dataset. We recommend that reconstructions also be performed using these transfer functions and the results compared. Given that some taxa have apparently different TN preferences in the different datasets we would expect the different transfer functions to produce different reconstructions. However, if downcore changes in diatom taxa are primarily driven by changes in TN concentrations then we would expect the three reconstructions to follow similar trajectories, even if they differed in the absolute values of the hindcast TN concentrations. If the three methods produce widely divergent reconstructions this would suggest that the core contains key taxa whose distribution is not primarily related to TN, and as such, the reconstructions should be treated with caution.

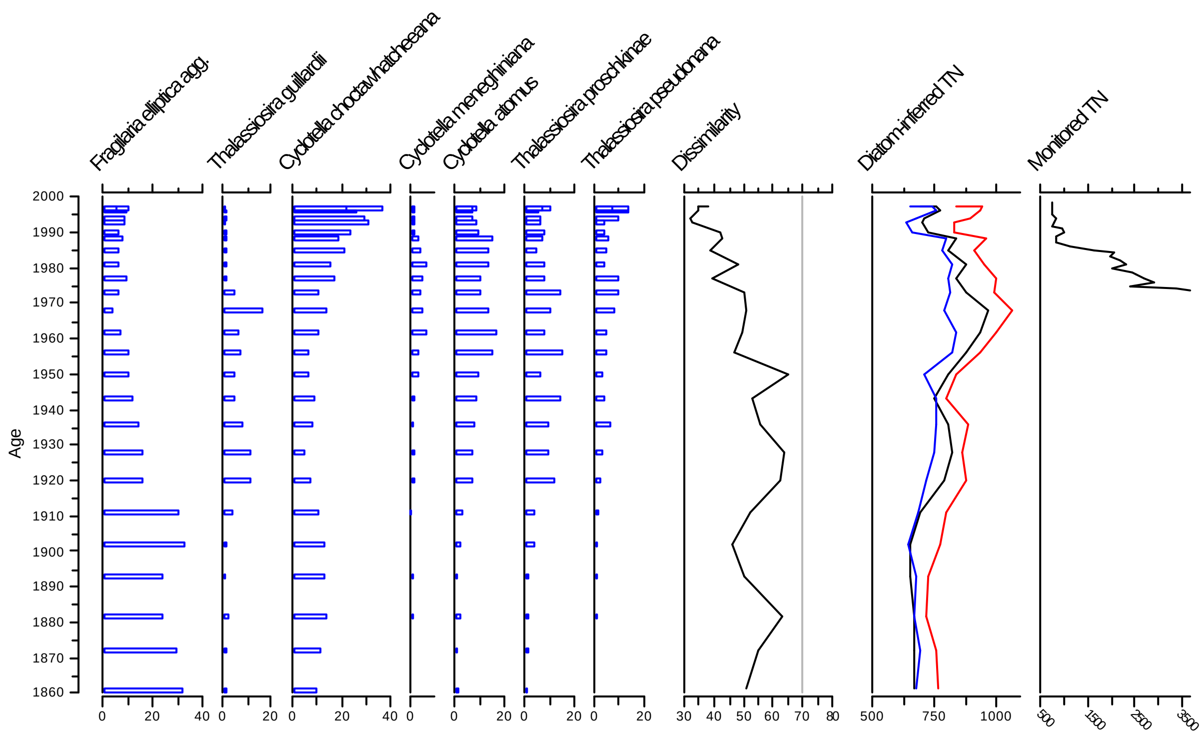
3. Validation against historical TN concentration measurements

The most robust evaluation of hindcast TN concentrations is to compare reconstructed values with historical time-series where these exist. Close agreement between hindcast and measured TN increases confidence in the reconstruction whereas divergence between the two sets of data warrants caution. However, close agreement during the monitoring period does not necessarily imply accurate reconstructions for earlier periods, especially if assemblages have very different composition. Conversely, divergence for the monitoring period does not necessarily imply reconstructions for earlier periods are in error.

8. Example of a palaeoecological reconstruction

The figure below shows the summary diatom stratigraphy from Laajalahti, together with analogue measures and TN concentrations hindcast using three different transfer functions. The diagram clearly shows the transition from a flora dominated by benthic *Fragilaria* taxa in the late 19^{th} century to one dominated by a succession of planktonic *Cyclotella* and *Thalassiosira* species today. All fossil samples have a squared chi-square dissimilarity less than 70, suggesting that they all have good floristic analogues in the Eastern Baltic training set. Hindcast TN concentrations using the Eastern Baltic transfer function show a steady increase from ca. 700 $\mu g\ l^{-1}$ in the late 19^{th} century to a maximum of 1000 $\mu g\ l^{-1}$ in 1970. After this date hindcast TN concentrations have fallen to ca. 700 $\mu g\ l^{-1}$ which compares well with the present observed value of 730 $\mu g\ l^{-1}$. In this example the TN values hindcast using the Eastern Baltic and combined Baltic WAPLS and LWWA transfer functions all show the same trajectory although they differ in absolute value for parts of the core. Comparison between the TN values hindcast using the Eastern Baltic transfer function and monitoring data for the last 30 years show that the transfer function is able to reproduce trends and absolute values for the last ca. 10 years but underestimates concentrations during the most eutrophic period during the 1970s. This underestimation is probably due to the lack of high TN sites in the training set.

Since all reconstructions follow the same trend we conclude that the main taxonomic changes observed in the core are driven by changes in TN concentration, and that the hindcasts made using the Eastern Baltic transfer function are the best estimate of historic trends TN concentrations. Comparisons with monitored data suggest that the hindcasts underestimate actual TN concentrations during the most eutrophic phase of the embayment but that periods of lower TN concentration are accurately reconstructed.



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