BOREAL ENVIRONMENT RESEARCH 7: 27–40
Helsinki 28 March 2002
ISSN 1239-6095

Diatom-inferred increase in limnetic phosphorus concentration and the associated changes in sedimentary phosphorus fractions in Valkjärvi, a lake in Kärkölä, Finland

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Kauppila, T., Moisio, T. & Salonen, V.-P. 2002. Diatom-inferred increase in limnetic phosphorus concentration and the associated changes in sedimentary phosphorus fractions in Valkjärvi, a lake in Kärkölä, Finland. *Boreal Env. Res.* 7: 27–40. ISSN 1239-6095

A diatom-based total phosphorus (TP) model developed for southern Finland is used to infer past epilimnetic TP concentrations in Valkjärvi, a lake located in Kärkölä, Finland; and the results are compared with sedimentary phosphorus fractions. The diatom-based models accurately predicted epilimnetic TP concentrations as indicated by monitoring data available since 1979. Altogether, concentrations have increased from 15 μg P l^{-1} in the 1940s to the present level of ~65 μg P l^{-1}. After an initial slow increase, the lake became eutrophicated rapidly in the 1960s as a result of municipal wastewater from the Kärkölä commune. These nutrient inputs resulted in increased sedimentary phosphorus concentrations. The NaOH-extracted phosphorus fraction in particular increased in the profundal sediments. The changes in sedimentary phosphorus nevertheless occurred later than the increase in diatom-inferred limnetic TP concentration.

Introduction

Eutrophication of lakes is a well-known environmental problem in many parts of the world and, after an initial debate over the nutrient mainly responsible for the phenomenon, phosphorus is now recognized as the factor that most frequently determines the level of increased production in many freshwater ecosystems (OECD 1982). As the deterioration in water quality associated with eutrophication is of economic importance, extensive attempts have been made to restore lakes to their original trophic state. Since no long-term monitoring data are usually available to define the background conditions of these lakes, palaeolimnological methods have proved invaluable for the study of their nutrient history.

Microfossil-based inference models, particularly ones employing diatoms (Bacillariophyceae), have been widely used to estimate past epilimnetic phosphorus concentrations in lakes (Hall and Smol 1999). Several diatom-total phosphorus (TP) models have been developed for various geographic areas during the last ten years, and their performance has been tested against measured limnetic concentrations in down-core applications, e.g. by Bennion *et al.* (1995), Marchetto and Bettinetti (1995), Hall *et al.* (1997), Rippey *et al.* (1997), Lotter (1998), Alefs and Müller (1999), and Kauppila *et al.* (2002), with encouraging results. It has been shown that sedimentary diatom assemblages can be used to reliably reconstruct past lake water TP concentrations and certain other environmental variables. It may partly be because of these recent advances that the use of palaeolimnology is included in the new EU Water Framework Directive (European Parliament and Council 2000) as one of the tools to determine reference conditions for different types of watercourse.

Another method used to trace eutrophication is the study of sedimentary phosphorus concentrations. In contrast to diatom models, sediment phosphorus cannot be used to reconstruct lake water phosphorus concentrations because of a number of complicating factors (Engstrom and Wright 1984). For instance, not all phosphorus in lake water is incorporated into the sediments, and the fraction that is eventually sedimented can change with time (Gibson *et al.* 1996). Furthermore, post-depositional mobility can lead to erroneous interpretations (Carignan and Flett 1981, Boström 1984, Itkonen and Olander 1997). Sediments nevertheless play an important role in lake metabolism as both a sink and a source of nutrients. Sedimentary phosphorus is an important phosphorus compartment in the lake system, and therefore analyses of sedimentary phosphorus are essential in applied palaeolimnological eutrophication studies.

In accordance with the importance of these two methods, a number of papers have been published that make use of both diatom-TP inferences and sedimentary phosphorus analyses (Anderson *et al.* 1993, Anderson 1994, Anderson and Rippey 1994, Bennion *et al.* 1995, Brenner *et al.* 1995, Brenner *et al.* 1996, Rippey and Anderson 1996, Hall *et al.* 1997, Rippey *et al.* 1997, Chen and Wu 1999). In all of these, total sedimentary phosphorus was analyzed. Additional information on phosphorus binding to sediment can be gained, however, by applying a chemical fractionation procedure (Pettersson *et al.* 1988), and attempts have been made to estimate the importance of such sedimentary phosphorus fractions as organic P, Ca-bound P, Fe and Al-bound P, labile P, exchangeable P, reductant-soluble P, and algal available P. Accordingly, various extraction schemes for the fractionation of sedimentary phosphorus have been developed (Pettersson *et al.* 1988, Jáuregui and García-Sánchez 1993).

This present study discusses changes in sedimentary phosphorus fractions, employing one of the commonly used extraction schemes, and their relation to the diatom-inferred increase in limnetic total phosphorus concentration in Valkjärvi, currently eutrophic boreal lake. Two short cores were taken from the lake and analyzed for diatoms and sedimentary phosphorus fractions to investigate the effect of coring location on these variables. Water chemistry data available for the lake since 1979 were used to check the observations, and an attempt was made to date a lake sediment sequence using soot particle stratigraphy and cyclicities in deposition detected by detailed grain-size analysis.

Sampling site

Valkjärvi is a lake located in Kärkölä, southern Finland, at approximately 25°15´E, 60°52´N (Fig. 1). It is currently eutrophic, with an average surface-water total phosphorus (TP) concentration of 65 μg P l^{-1} in the 1990s. The lake has an area of 1.5 km^2 and a catchment of 22.5 km^2. It is a single-basin lake with a maximum depth of 10.5 m. Surface sediments in the catchment consist of glaciolacustrine clays, some peat bogs and glaciofluvial deposits with a few outcrops of Precambrian bedrock surrounded by till. Most of the clay area around the lake is cultivated and there are both holiday cottages and permanent houses close to the shoreline. The brook of Pyhäoja runs into the lake from Kärkölä (Fig. 1).

Material and methods

Valkjärvi was sampled in January 1997 with a wedge-shaped crust freeze corer (Renberg 1981). The core KVALK 297 was taken from the deepest part of the lake (9.5 m), and KVALK 397 from a location close to the inlet of the brook Pyhäoja in a water depth of 1.7 m (Fig. 1). This location was also cored with a Russian-type corer (Jowsey 1966) to examine the sedimentary structures. The cores were inspected visually and described in the field according to the method of Troels-Smith (1955) and using a Munsell® colour chart. The frozen cores were then wrapped in metal foil and plastic, transported to the laboratory in a frozen state, and stored at –18 °C.

To investigate the possible cyclical nature of sedimentation at the brook mouth, the core KVALK 397 was subsampled with a scalpel in continuous 1 mm slices and analysed for the grain-size distribution of inorganic matter. Prior to the analysis, organic matter was digested with H_2O_2 and aggregates were disintegrated by low-power ultrasonication (2 h). The samples were analyzed using the Coulter Electronics LS 200 laser particle sizer.

The mean, median, and modal grain-sizes of approximately 400 grain-size distributions were used in time-series analyses by autocorrelation, partial autocorrelation and spectral analysis. The analyses were performed after removal of any linear trend in the data and subtraction of the overall mean using a five-observation Hamming window for spectral density estimates. All the time series analyses were performed using STATISTICA 5.0 software.

The soot particle stratigraphy of both cores

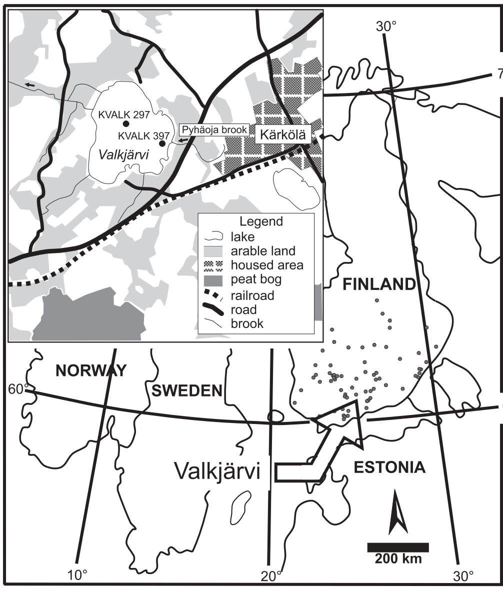

Fig. 1. Map of Valkjärvi and its location in Fennoscandia. Grey dots on the large map = calibration set lakes, black dots on the inset map = coring sites.

was analyzed in continuous 1-cm slices. Soot particles, or spherical carbonaceous particles (SCP), originating from fossil fuel combustion have a characteristic shape and can be identified using a light microscope (Rose 1990). Their distribution in a sediment core can be compared with the known history of fossil fuel consumption for the region to date the sediment sequence. Data on annual oil and coal consumption for Finland were obtained from the State Technical Research Centre (VTT). Only fuel types causing SCP emissions were included in the statistics.

As SCP are almost entirely composed of elemental carbon (Wik and Natkanski 1990), they are chemically inert, and they can, therefore, be separated out for microscopy by removing all other sediment components by sequential chemical attacks. The method used is a modification of that of Rose (1990) involving oxidation with H_2O_2, acid digestion with HCl, removal of silicates with HF and another HCl digestion to remove any calcium fluoride crystals formed in the HF step. A known amount of *Lycopodium* spores was added to the sample after the oxidation step to facilitate quantitative counting of the soot particles. The slides were mounted with Naphrax® and studied under a Leitz Dialux 20EB microscope at 400× magnification. To avoid bias in the counting procedure, all the slides were recoded so that no indication of sediment depth was visible on them. All the counts included at least 200 *Lycopodium* grains. The SCP and grain-size data have been discussed earlier by Kauppila *et al.* (2002), but the results will be examined more thoroughly here based on historical information about disturbances in the lake.

Subsamples for the diatom analyses were taken in 0.5 cm slices at 1.5 cm intervals and treated with H_2O_2 to oxidize organic matter and washed three times with distilled water to remove the oxidant. A drop of the resulting suspension was dried on a coverslip at room temperature and the dried coverslip mounted with Naphrax®. A minimum of 300 valves were identified on each slide, mainly using Krammer and Lange-Bertalot (1986–1991) as reference. Author citations are included for taxa not named according to this reference work. The microscope used was a Leitz Orthoplan with a 100× Plan Apo oil immersion phase objective (n.a. = 1.32) and 12.5× eyepieces. The diatom results for KVALK 297 have been published earlier in Kauppila *et al.* (2002). These previous observations will be re-evaluated here by different methods and compared with the results of core KVALK 397.

The calibration data set used for the TP reconstructions has been described by Kauppila *et al.* (2002), who developed a weighted averaging partial least squares (WA-PLS) inference model for the autumnal lake surface water TP concentration. The 61-lake data set making up their final model was used in the present study to develop four separate WA-based models for TP (inverse and classical deshrinking, with and without tolerance downweighting). The data consist of surface sediment diatom counts and mostly autumnal circulation period water chemistries for lakes in the southern part of Finland (Fig. 1) and have a TP range of 3–89 μg P l^{-1}. Valkjärvi lies, therefore, at the upper end of the calibration set TP gradient. The models were developed with the CALIBRATE 0.85 software of S. Juggins and C.J.F. ter Braak (1997, unpublished software).

The suitability of the calibration dataset for reconstruction of TP from fossil diatom assemblages was assessed using constrained ordinations and analogue matching performed using the programs CANOCO version 4.0 (ter Braak & Šmilauer 1998) and MAT (S. Juggins, unpublished software), respectively. The response of the assemblages to gradients other than TP, indicated by a lack-of-fit of the fossil samples with TP, was studied by entering them as passive samples in Canonical Correspondence Analysis (CCA), constrained to TP. Samples with a squared residual distance from the TP axis that was longer than the extreme 5% of distances of the training set samples were considered to have a poor fit to TP. Samples having poor analogues in the calibration set were defined as those having a squared chord distance to the closest sample in the calibration set that was larger than 0.44, corresponding to the fifth percentile of the distances between all training set samples. Samples with a minimum distance larger than 0.51 (tenth percentile) were regarded as having very poor modern analogues.

The phosphorus fractionation procedure, modified from Hieltjes and Lijklema (1980), involved sequential extractions with H_2O, 0.1 M NaOH and 0.5 M HCl and subsequent analysis by the molybdenum blue method of Murphy and Riley (1962). Separate subsamples were taken for total phosphorus determination by the molybdenum blue method after digestion of the ignited samples with HNO_3 and HCl (Bengtsson and Enell 1986). In addition, the water content of the samples was determined as weight loss after drying overnight at 105 °C and loss-on-ignition after ashing the sample at 550 °C for 2 h.

The H_2O extraction result is considered to represent labile phosphorus (H_2O-P), while NaOH extracts phosphorus bound to short-range ordered Fe and Al hydroxides and organic complexes that is exchangeable for OH^- (NaOH-P). This fraction is considered critical for internal loading since the reduction of Fe(III) to Fe(II) associated with seasonal anoxia in eutrophic lakes often results in remobilization of phosphorus in sediment (Boström *et al.* 1982, Psenner 1984). In contrast, the HCl-extracted phosphorus (HCl-P), often called Ca-phosphorus, is bound to carbonates and apatitic minerals and is not liberated under reducing conditions. Due to its largely mineral nature, this fraction is frequently of importance in littoral sediments (Boström *et al.* 1982). The residual fraction is obtained as the difference between total phosphorus content and the sum of all fractions and represents mainly phosphorus in refractory organic material (Pettersson *et al.* 1988).

The municipality of Kärkölä has gathered water monitoring data for Valkjärvi, largely through the agency of environmental consulting companies that have been responsible for taking the samples and analyzing them over the years. The determinations have been carried out according to accepted standards for the analysis of fresh water. In practice, total phosphorus analysis involved peroxodisulfate digestion and photometric determination using the molybdenum blue method (e.g., Suomen standardisoimisliitto SFS ry. 1986)

Results and discussion

Lithology

The core taken from the deepest part of the lake (KVALK 297), 77 cm in length, consists of homogeneous silty gyttja up to the 28 cm level (Fig. 2). The sediment section is dark olive green in colour, as is typical for lakes in southern Finland with high autochthonous production and a clay overburden in their catchment. Dark sulphide laminae appear in the sediment at approximately 28 cm, but the structure is too uneven to allow any estimates of sedimentation rate to be made even if the stripes were formed annually. The sulphide-coloured section continues up to the top of the sediment, indicating that reducing conditions have occurred intermittently in the upper sediment layer for several years now.

At the littoral KVALK 397 site, the additional sampling with a Russian-type peat corer allowed penetration of the lake sediment sequence down to the underlying laminated silty clay. The gyttja resembles that of the KVALK 297 core but is slightly richer in silt and is thus lighter in colour. Despite the different sedimentary environment and the slight difference in the appearance of the gyttja, sulphide stripes become visible in KVALK 397 at approximately the same level as in the deep-water core (29 cm), but the loose top section found in KVALK 397 is lacking in KVALK 297.

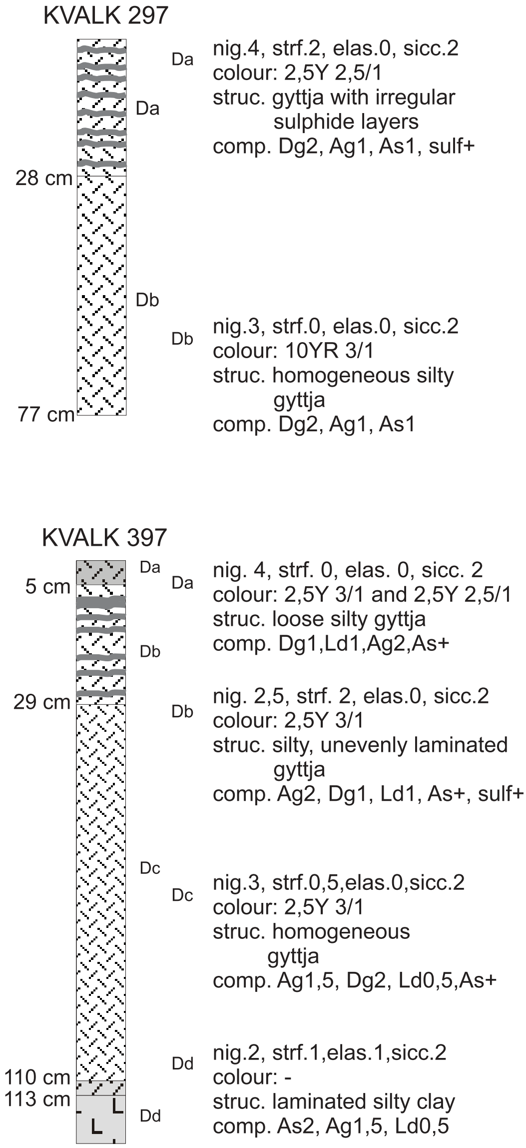

Fig. 2. Core lithologies according to the Troels-Smith system. Da-Dd = loci descripti. The graphical symbols do not conform to Troels-Smith (1955).

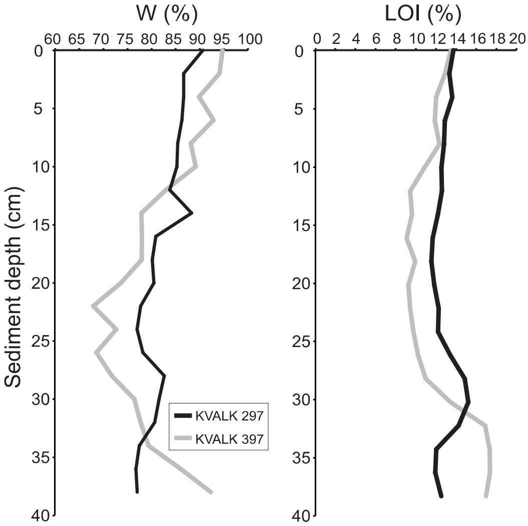

Fig. 3. Vertical distribution of water content and percentage loss-on-ignition (LOI) in the cores. Black = KVALK 297, grey = KVALK 397.

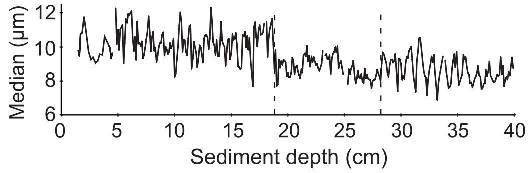

Fig. 4. Grain-size analysis results (median) for core KVALK 397. Dashed lines mark the section boundaries used in time series analysis.

Loss-on-ignition and water content

Loss-on-ignition (LOI) and water content (W%) profiles for the sediment section between 0 and 40 cm are presented for both cores in Fig. 3. There is a section of increased LOI and W% between 36 and 27 cm in KVALK 297, whereas LOI declines rapidly between 28 and 32 cm in KVALK 397 and the water content decreases immediately from 40 cm. There is a section of low LOI and water content above 27 cm in both cores, with a subsequent increase towards the sediment surface, probably due to increased productivity and to ongoing compaction and organic matter mineralization.

Grain size and soot particles

The results of the grain-size analyses are presented in Fig. 4, which displays the variation in median grain size (μm) in core KVALK 397 for the top 40 cm. The mean and modal grain size (not shown) produce similar results. The profile can be divided into three sections with differing characteristics. The first section ranges from 40 cm to 28 cm and is characterized by a regular fluctuation in median grain size around 8.5 μm. The amplitude of these cycles increases upwards and an abrupt decrease in amplitude marks the beginning of the second section at 28 cm. In this section, extending to 19 cm, the average median grain size is approximately similar to that of the lower section but the variations are less regular and the size range is smaller. In contrast, the uppermost section is characterized by coarser material and large variation. The transition at 19 cm is again an abrupt one.

The estimation of deposition rates was based on cyclicities in the grain size of the deposited inorganic matter. As expected from examination of the grain-size curve (Fig. 4), a cyclicity was identifiable for the deepest sediment section by all three time series analysis methods employed. Assuming that one cycle corresponds to one year's deposition, all the methods suggested a deposition rate of 10 mm a^{-1} for this seemingly structureless section between 40 and 28 cm. In contrast, there was no agreement between the methods for the mid-section. A deposition rate of 7 mm a^{-1} will be used for the 28–19 cm section in the following discussion, based on partial autocorrelations and, to a lesser extent, autocorrelations. Similarly, the deposition rate of 8.5 mm a^{-1} inferred for the 19–0 cm section is based on the somewhat differing cyclicities detected by the three methods. Lags of 8 and 9 mm had the highest partial autocorrelations for the median and modal grain sizes, the highest autocorrelations being associated with lags of 9 and 10 mm, and spectral analysis suggested a period of 9.5 mm for this topmost section. The selected estimate is thus a consensus figure based on all three methods.

Soot particle dating was used to support the

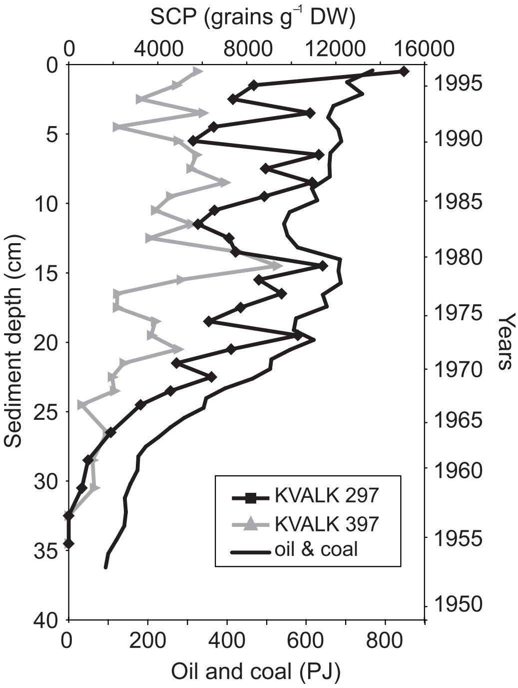

Fig. 5. Soot particle profiles for cores KVALK 297 and KVALK 397. Yearly consumption of SCP-producing forms of oil and coal in Finland is expressed as energy (PJ = petajoule). The year scale is based on the estimated deposition rates. Modified from Kauppila *et al*. (2002).

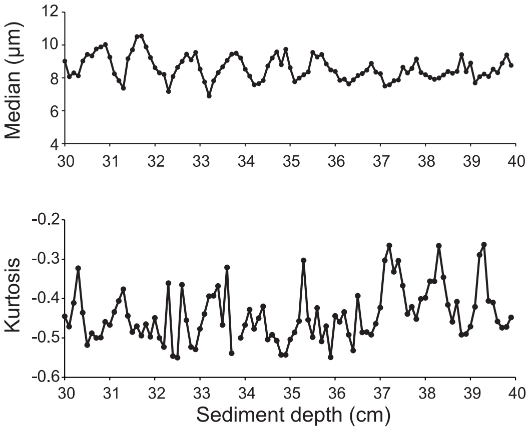

Fig. 6. Median and kurtosis for the grain-size distributions in samples between 30 and 40 cm depth in KVALK 397, showing the change at 37 cm.

grain-size inferred deposition rates. The results of SCP analysis for both cores are presented in Fig. 5. The profiles are broadly similar, with soot particles appearing at 31 cm, after which the concentration rapidly increases. The most marked increase in fossil fuel consumption in Finland occurred in the 1960s, and can be detectable with SCP to date the sediments (*see* Tolonen *et al*. 1990). The SCP concentrations are higher in KVALK 297 and the curve less noisy, presumably because of the funnelling effect that deposits more soot at the deepest point of the lake. The KVALK 297 profile is therefore easier to compare with the statistics of annual oil and coal consumption in Finland (Fig. 5). In view of the similar lithologies of the two cores and the appearance of SCP at the same level, the fossil fuel consumption curve has been fitted to both SCP profiles using the grain size-inferred deposition rates for KVALK 397. The resulting fit is good, lending support to the estimated deposition rates.

The use of detailed grain size analyses thus appears to facilitate deposition rate estimates under favourable conditions. The inferred deposition rates for KVALK 397 are not unambiguous, however, and neither of the prominent changes in grain size can be dated to 1952, a year with known disturbances (dredging of the Pyhäoja brook and the beginning of lake level regulation). Instead, the 1952 sediment level falls at 37 cm, just below the changes in LOI and water content. These changes could have resulted in more minerogenic matter being deposited at the brook mouth and a pulse of organic-rich sediment being redeposited from near-shore areas into the deeper parts as a consequence of water level regulation. Furthermore, the median grain size increases slightly at the same level, the cyclicity in kurtosis disappears, and the grain size distributions become less peaked overall (lower kurtosis, *see* Fig. 6). These changes may also be related to the 1952 disturbances, but the shift in modal grain size observable at 19 cm remains unexplained. The irregularity in the grain size curve that begins at 28 cm, on the other hand, may be related to sulphide grains, as sulphide colouring appears in the sediment at this level.

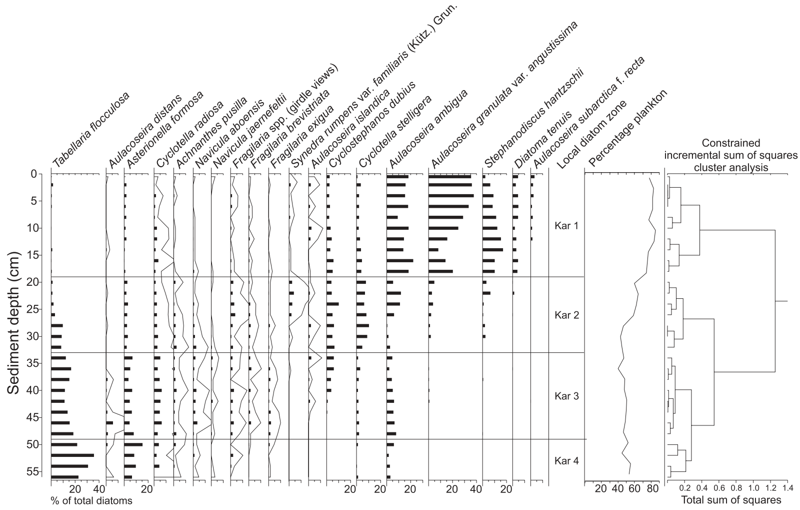

Fig. 7. Distribution of selected diatom taxa in the profundal KVALK 297 core. Solid line = 5× exaggeration. Plankton percentage is also shown. Modified from Kauppila *et al*. (2002).

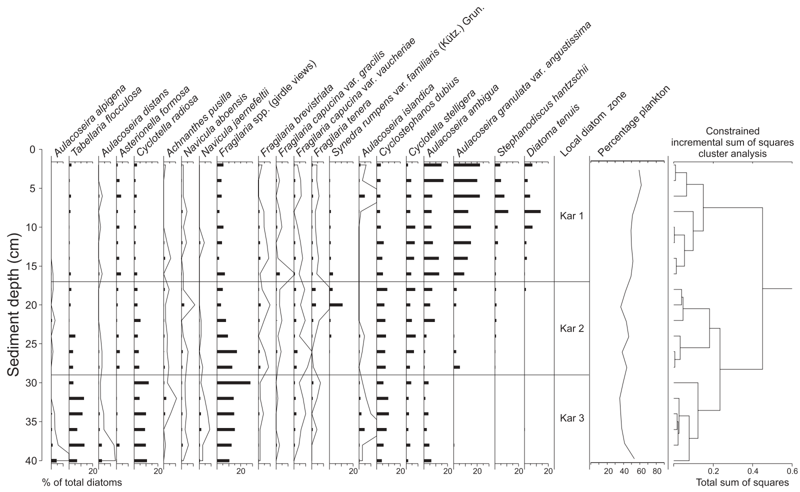

Fig. 8. Relative abundances of selected diatom taxa in the littoral KVALK 397 core. Plankton percentage is also shown. Solid line = 5× exaggeration.

Diatoms

The relative abundances of selected diatom taxa are shown in Figs. 7 and 8 (KVALK 297 and 397, respectively). The dendrograms, produced with CONISS software, which uses the incremental sum of squares method for stratigraphically constrained cluster analysis (Grimm 1987),

Table 1. Jack-knifed estimated model parameters for the four models used in the reconstruction. RMSEP = root mean squared error of prediction.

Deshrinking	Model	RMSEP (log µg P l^{-1})	R^2	Max. bias (log µg P l^{-1})
Inverse	WA	0.1604	0.7586	0.2747
Inverse	WA tol	0.1691	0.7350	0.2939
Classical	WA	0.1673	0.7632	0.1309
Classical	WA tol	0.1704	0.7411	0.1555

are also shown. The 40 most abundant taxa were used for clustering, and local diatom zones (L.D.Z.) were determined on the basis of the analyst's interpretation of the diatom distributions and the dendrogram.

The major species shifts are the same in both diagrams. The lower section of both cores is characterized by high abundances of *Tabellaria flocculosa*, *Aulacoseira distans* and *Cyclotella radiosa,* whereas *Aulacoseira ambigua*, *Aulacoseira granulata* v. *angustissima*, *Stephanodiscus hantzschii* and *Diatoma tenuis* predominate in the Kar 1 zone. The proportions of major taxa also increase at corresponding levels in both cores. Despite these similarities, the differences caused by contrasting coring locations (littoral vs. pelagic/profundal) are manifested in terms of a higher relative abundance of planktonic taxa in KVALK 297 and abundant benthic *Fragilaria* in KVALK 397. *Aulacoseira subarctica* f. *recta,* for instance, increases in zone Kar 1 in KVALK 297 but not in the littoral core.

The dominance of eutrophic planktonic taxa in the Kar 1 zone results in a decline in the relative abundances of periphytic *Achnanthes*, *Navicula* and *Fragilaria* taxa that are present throughout the cores. Logically, the effect will be stronger in the profundal KVALK 297 core. The taxon named here *Synedra rumpens* var. *familiaris* (Kütz.) Grunow is present only in the upper parts of the diagrams. It increases to its maximum relative abundance at the top of zone Kar 2 in both cores, but declines to very low levels in the Kar 1 zone.

Inference model and calibration

The data set used for developing the inference models is described in more detail by Kauppila *et al*. (2002), who show by means of constrained and partially constrained ordinations that it is possible to reconstruct TP from fossil assemblages using the available data. The inference models developed here are WA models with and without tolerance downweighting, using both classical and inverse deshrinking (classWA, classWAtol, invWA, invWAtol, Table 1) with log-transformed TP concentrations. As expected, the inverse deshrinking models have lower root

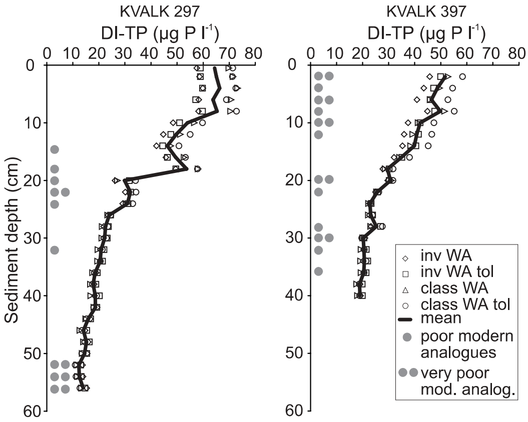

Fig. 9. Diatom-inferred epilimnetic phosphorus concentration profiles for the KVALK 297 and KVALK 397 cores. Results obtained with all four models (weighted averaging using classical and inverse deshrinking, with and without tolerance downweighting) and their means are shown.

mean squared errors of prediction (RMSEP) than the models with classical deshrinking (ter Braak and Juggins 1993) but have substantially larger maximum bias.

The calibration results are shown in Fig. 9, with curves to represent the means of the four diatom-inferred TP values. In KVALK 297, the reconstructed TP concentration remains at 15 μg P l^{-1} between 56 and 44 cm, increasing gradually to 25 μg P l^{-1} at the 25 cm level. Thereafter, DI-TP increases rapidly until the values stabilize around 65 μg P l^{-1} at 8 cm. In contrast, the increase in DI-TP is less marked in KVALK 397 and no levelling out of the trend is seen at the top. The DI-TP concentrations in the upper section are 10 μg P l^{-1} lower for KVALK 397 than for KVALK 297.

The lower predicted TP concentration in the littoral core is due to the higher number of periphytic taxa in the samples. Due to their high limnetic nutrient concentration, eutrophic lakes have a high planktonic diatom abundance, which causes a corresponding lowering in the relative proportion of benthic diatoms in surface sediment samples. The weighted averaging-based regression methods may, therefore, assign too low TP optima for the periphytic taxa. However, this need not always be the case as non-planktonic taxa of especially the genus *Fragi-*

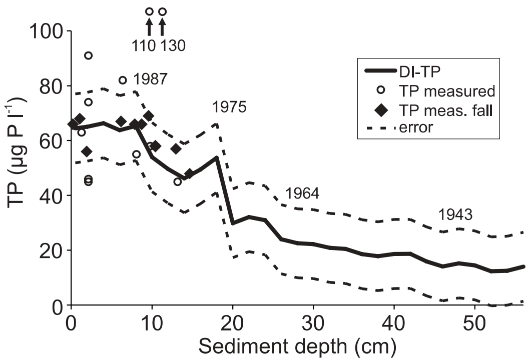

Fig. 10. Diatom-inferred TP profile for the KVALK 297 core. The measured epilimnetic TP concentrations are placed in the figure using the estimated deposition rates. Dashed lines = mean 'error' of prediction (*see* text), arrows = late winter TP measurements in 1984 and 1986.

laria have in some sets been observed to occur along the whole length of the TP gradient (Bennion 1995, Bennion *et al.* 2001). Therefore, such taxa will be assigned TP optima close to the centre of the gradient available and, depending on the characteristics of the calibration set and the target lake, this can lead to TP overestimation (Bennion *et al.* 2001).

There are also differences between the cores in the predictions given with the four models. Marked differences in DI-TP are obtained using classical and inverse deshrinking above ~30 μg P l^{-1} in both cores, because these types of model have differing trends in their residuals.

Assessed by CCA constrained solely to TP, only one sample, at 20 cm in KVALK 397, exhibited a poor fit to TP as it had a residual distance from the TP axis longer than the extreme 5% of the distances among the training set samples. However, some samples lacked modern analogues in the training set. In Fig. 9, samples with poor modern analogues are marked with a single dot and samples with very poor modern analogues with two dots.

The modern analogue data also highlight the differences between the cores, as most of the KVALK 397 samples lack modern analogues. This presumably results from the littoral coring location, as the training set represents cores from central lake locations. The KVALK 297 coring site is therefore more appropriate than KVALK 397 for calibration purposes using the present data set. The reason for the concentration of poor modern analogues in the section immediately above 25 cm in both profiles apparently lies in the occurrence of *Synedra rumpens* var. *familiaris* (Kütz.) Grunow at higher percentage abundance than in any calibration set lake. The section is thicker in KVALK 297, as is also evident from the diatom stratigraphy (Fig. 8). Similarly, the lack of modern analogues at the base of the KVALK 297 core probably results from the high proportion of *Tabellaria flocculosa*.

The diatom-inferred TP for the KVALK 297 core, expressed as the mean of the values obtained using the four calibration methods, was compared with the available epilimnetic TP measurements (Fig. 10). The prediction error shown in Fig. 10 (12.6 μg P l^{-1}) was calculated as the mean error of prediction using the mean for the four jack-knifed inference models and back transformed log TP concentrations. This error is a considerable one, but much smaller than the annual range of epilimnetic TP concentrations in Valkjärvi (45 μg P l^{-1} in 1994). Understandably, the diatom-based model does not predict the very high concentrations, such as those measured in April 1984 and 1986 (shown by arrows in Fig. 10), but DI-TP does follow the autumnal measured TP values closely (diamonds in Fig. 10). This is to be expected, as the model was developed using autumnal circulation TP concentrations. The increase in lake surface water TP between 1979 and 1987 and the subsequent stabilization are faithfully recorded in the DI-TP results. The close match between measured and inferred TP also indirectly supports the deposition rate estimates discussed earlier. In addition, the mean of the four WA models is a more accurate predictor of the measured TP than the WA-PLS 1 component model described by Kauppila *et al.* (2002) which here corresponds to the invWA model.

The results indicate that Valkjärvi has not always been eutrophic. The increase in nutrient concentrations started in the 1940s and intensified in the mid-1960s. Agriculture was probably responsible for the initial, slow increase in DI-TP, whereas the rapid change in the mid-1960s was caused by municipal wastewater from

Kärkölä. A sewer system was built in Kärkölä in 1961, conducting untreated wastewater into the Pyhäoja brook. The rapid eutrophication phase was probably intensified by seasonal anoxia at or slightly below the sediment-water interface, as evidenced by the appearance of sulphide laminations in the sediment. From 1975 onwards, however, the wastewater was directed to a treatment plant located downstream of Valkjärvi, and this may have caused the temporary drop in diatom-inferred TP at 18 cm, although it did not reverse the increase in lake water phosphorus concentration. This probably reflects the importance of diffuse and internal phosphorus loading sources for lake eutrophication.

However, the diatom-inferred TP stabilizes above 10 cm despite some changes in the proportions of major taxa, since all these taxa have similar TP optima. Due to the large scatter, no levelling out of nutrient concentrations after 1987 is evident from the monitoring data, when taken as a whole, but the autumnal measured TP concentrations do not increase after this period and extremely high nutrient concentrations (> 100 μg P l^{-1}) have not been measured since 1986. The reason for this pattern cannot lie in restoration efforts, which were started only in 1993, although the proportions of *Aulacoseira granulata* var. *angustissima* and *Stephanodiscus hantzschii*, both taxa with high TP optima (46.2 μg P l^{-1} and 35.5 μg P l^{-1}, respectively), decrease slightly in the topmost samples.

Sedimentary phosphorus fractions

The sedimentary phosphorus fractionation results are presented in Fig. 11. The total phosphorus concentrations are comparable and increase upwards in both cores, whereas the H_2O-leached fraction is low in all the samples. There is a rapid increase in NaOH-P at 15 cm in KVALK 297, with a simultaneous but smaller increase in HCl-P, whereas both HCl and NaOH-extracted phosphorus increase above 15 cm in KVALK 397, with the HCl fraction dominant in all the samples. This is to be expected, as littoral sediments often contain relatively much Ca-bound phosphorus (Boström *et al.* 1982). The section of increased total phosphorus between 37 and 29 cm

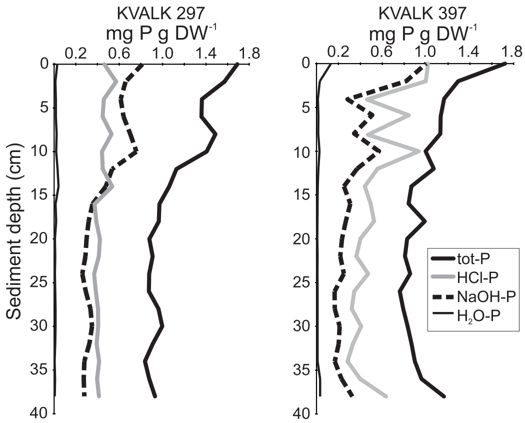

Fig. 11. Vertical distribution of sedimentary phosphorus fractions in the Valkjärvi cores.

in KVALK 297 results from the elevated organic matter content (Fig. 3), presumably caused by the lake level regulation. The change is observable in the NaOH fraction (Fe-bound P) since much of this phosphorus is bound to Fe(III)-organic matter complexes (Pettersson *et al.* 1988).

Sedimentary phosphorus concentrations begin to increase later than the diatom-inferred TP rise. The slow initial increase in epilimnetic phosphorus concentration, as inferred from the diatom data, from 40 cm sediment depth, did not cause any increase in sediment phosphorus content or any change in the relative proportions of the phosphorus fractions. It is not until 15 cm that the total phosphorus concentration and the proportion of labile NaOH-P both increase, approximately ten years after the diatom-inferred limnetic phosphorus concentrations began to increase more rapidly. There appears, therefore, to be a delay between nutrient enrichment and the increase in sedimentary phosphorus. Aquatic biota are able to assimilate and recycle an increased amount of nutrients in the water column, thereby delaying any increase in phosphorus sedimentation, but the sedimentation of phosphorus inevitably increases as limnetic concentrations rise further.

The sedimentary total phosphorus concentration between 3 and 13 cm in KVALK 397 does not increase together with HCl-P and NaOH-P as it does in KVALK 297, and the total phosphorus concentration is less than the sum of the fractions in four samples (Fig. 11). Excluding the possibility of error in the analysis, this phenomenon may be related to a change in the composition of sedimentary phosphorus that has caused a decrease in the residual phosphorus fraction and lessened the efficacy of the acid leaching used in total phosphorus determination. In any case, it renders the total phosphorus determination for the upper section of KVALK 397 unreliable.

The increase in total phosphorus and NaOH-P in KVALK 297 is interrupted by a depression at ~5 cm not observable in the HCl fraction. This is probably caused by post-depositional mobility of phosphorus in the sediment, as the changes are greatest in the NaOH fraction. It is this fraction that becomes mobilized with a lowering of the redox potential in the sediment and a reduction of Fe(III) to Fe(II) (Boström *et al*. 1982). The topmost sediment still binds phosphorus, however.

Conclusions

The results show that high-resolution grain-size analyses can be used for approximate lake sediment dating even when the sediment looks homogeneous. In the present study the proximity of the coring location to an inlet and a high deposition rate contribute to the success of the approach.

Diatom-inferred total phosphorus concentrations followed the measured concentrations closely and indicated that nutrient levels in Valkjärvi have increased considerably since 1940. In fact, the inferred TP levels span almost the whole TP range of the lakes in the calibration set. The initial increase was slow and probably related to intensified agriculture after the war, whereas municipal wastewater caused more rapid eutrophication in the 1960s. The limnetic TP concentration continued to increase even after diversion of the wastewater, however, because of internal lake processes and/or loading from other sources.

The diatom-based inferences for the littoral core differ from those for the pelagic core, with lower inferred TP concentrations and fewer modern analogues for the former. Both features result from the fact that cores were taken from central lake locations in the training set. Thus littoral diatoms are poorly represented in the surface sediments of the nutrient-rich calibration set lakes, leading to their being assigned low estimated TP optima. It is perhaps unsurprising that a calibration set based on sediment samples from the central area of lakes will not provide good analogues for diatom assemblages found in littoral cores.

As expected, sedimentary phosphorus concentrations increase with the phosphorus concentration in the lake water, but there is a delay in the response, as small initial increases in limnetic [TP] are not reflected in sedimentary phosphorus. Nutrient recycling appears to delay the increase in phosphorus sedimentation, but once the increase does happen, the fractional composition of the sediment phosphorus also changes, especially in the profundal core. Most of the increase is in NaOH-extracted phosphorus, the fraction susceptible to remobilization under reducing conditions. Indeed, there are signs of post-depositional mobility in the uppermost sediment layers in the profundal core, which makes interpretation of the sedimentary phosphorus profiles difficult.

Finally, the results highlight the importance of combining several approaches in sediment-based eutrophication studies. Explanations for observed patterns are more likely to be found using multiple analyses, and a well-selected package of analyses can convey a wealth of information needed for lake restoration purposes and for evaluating the current status of lakes.

Acknowledgements: The authors wish to extend their thanks to the Maj and Tor Nessling Foundation for its financial support for the first phase of the project. The diatom-based calibrations were made possible by a grant to TK from the Emil Aaltonen Foundation. We also wish to thank all those who helped with the fieldwork, and also Riitta Hyytiäinen and Jaakko Airola in Kärkölä for all their practical help and discussions. Malcolm Hicks and Emily Bradshaw reviewed the English of the manuscript.

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Received 28 June 2001, accepted 29 October 2001