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Assessment of pollution history from recent sediments in Lake Vanajavesi, southern Finland. I. Selection of representative profiles, their dating and chemostratigraphy

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79 short sediment cores were taken from surficial sediments of eutrophicated Lake Vanajavesi, which for a hundred years has been under pressure by waste water loading, mainly from the wood-processing industry. The grain-size distribution, water, organic and zinc contents were analyzed from the uppermost centimetre of these cores in order to map the surficial sediments and to locate representative coring sites. The standard deviation of the grain-size distribution of the surficial minerogenic matter was the most useful parameter indicating the dynamic energy level of the overlying water layers. Unexpected current activity was noted in the deepwater area and the area of accumulation bottoms was small. Four cores were selected from the accumulation bottoms for detailed investigations.

Of the analyzed heavy metals, zinc, cadmium and copper showed clear enrichment in the selected profiles. For these elements the max. cultural enrichment factors were 84.6, 6.1 and 2.9, respectively. Zinc was the best tracer for mapping the areal distribution and for giving historical records of industrial waste waters due to the high point-source loading from the chemical industry that has occurred since 1943. Analyses of the dehydroabietic acid content in sediment indicated an abrupt increase since the 1940s in the loading from the wood-processing industry.

To check the sedimentation and mixing conditions and the dating possibilities the distribution on ^{137}Cs, ^{239,240}Pu and ^{210}Pb was determined from four profiles. One of them was partly annually laminated, giving an accurate time scale since 1957. In this case dating based on ^{137}Cs and ^{210}Pb (constant initial concentration model, C.I.C.) agreed well with the varve chronology.

Other profiles were strongly mixed mainly due to the bioturbation, which decreased the time resolution of historical events. In these cases it proved possible to estimate the mean sedimentation rates (54-72 mg dry matter /cm^2/a), mixing depths and time resolution of the cores using the steady-state mixing model of ^{210}Pb distribution. Due to mixing, the peak of ^{137}Cs and ^{239,240}Pu was deeper than expected on the basis of mean sedimentation rate. The time scale derived from ^{137}Cs and ^{239,240}Pu distribution was in accordance with the zinc stratigraphy and known history of zinc loading.

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Contents

1. Introduction

Palaeolimnology is generally considered as the study of lake development in the past, e.g. during the whole post-glacial period. Palaeolimnological methods may also be used in the study of recent environmental changes, as well as those occurring at the present day. Chemical analyses of the content of nutrients, heavy metals and organic compounds in surficial sediments and short cores have been used in attempts to map the areal distribution and to provide an historical record of the emission of pollutants due to human activities (cf. Förstner & Wittmann 1979, Håkanson 1981a). Subfossils of diatoms, cladocers and aquatic insects can also be used as biostratigraphic indicators of recent eutrophication (e.g. Granberg 1972, Ravera & Parise 1978, Wiederholm & Eriksson 1979, Simola 1983) or acidification (e.g. Renberg & Hellberg 1982, Tolonen & Jaakkola 1983). The opportunities offered by sediment investigations however, have as yet been imperfectly exploited in the field of aquatic pollution control (Håkanson 1981a).

The palaeolimnological research carried out in Finland was reviewed by Alhonen (1979). During the last few years much progress has been achieved in the study of annually laminated lake sediments (e.g. Saarnisto et al. 1977, Tolonen, M. 1978, Vuorinen 1978, Tolonen, K. 1980 and Simola 1977, 1979, 1983). These sediments are ideal for studies of environmental changes. The occurrence of annually laminated sediments is limited, however, to conditions in which the rhythmic structure is preserved due to the lack of mechanical and biological disturbances. Studies of laminated sediments have greatly increased our knowledge of sediments and sedimentation processes and thereby enable us to draw more valid conclusions on normal, homogenous lake sediments (Renberg 1979).

The aim of this study is to apply and test sedimentological and palaeolimnological methods in the monitoring of a typical Finnish watercourse polluted by the wood-processing and chemical industry and by municipal sewage. As in aquatic pollution control in general, the primary object of interest is the recipient itself, i.e. the limnological changes which have led to the present stage of eutrophication and pollution. The time period of interest is the last 100-150 years, which is the industrial period in the history of Lake Vanajavesi.

There are important methodological questions requiring to be resolved before the 'information bank' stored in sediments can be

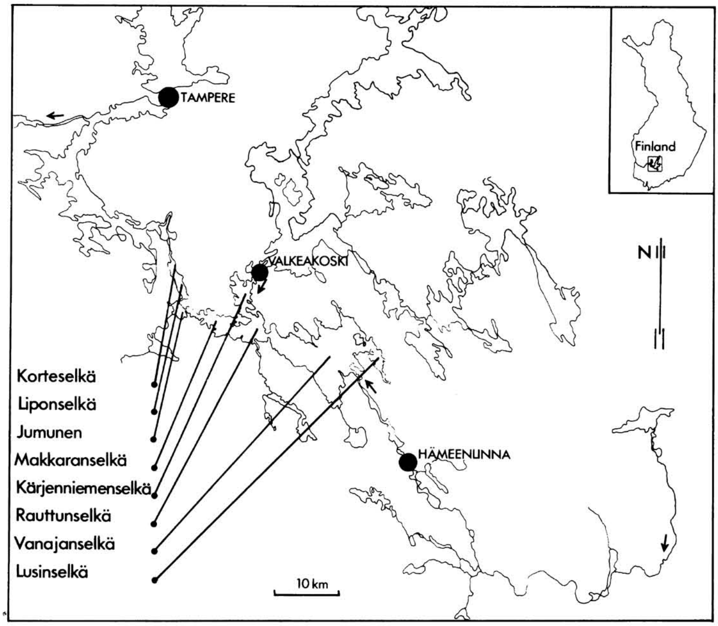


Fig. 1. The southern part of the drainage basin of the River Kokemäenjoki and location of the study area (shaded area). The direction of the water flow is indicated by arrows.

used. It is often difficult to find ideal sampling points at which the sediment layers are undisturbed and suitable for varve chronology. In large and morphologically complex lakes the physical disturbances (wave action, currents) may greatly limit the area of accumulation bottoms. In non-laminated sediments accurate dating may be difficult. In this case we have to use radiochemical methods based, e.g. on the distribution of ^{210}Pb and artificial radionuclides, to assess the sedimentation rate and the age-depth distribution of the sediment profiles necessary for the reliable interpretation of the sedimentary record of the lake development.

In the present part of the study the main emphasis is laid on the following methodological questions:

1) Which are the most useful sediment parameters for determining the bottom dynamic status at the sampling site; what information is needed in selecting representative profiles?

2) Which is the most reliable method of dating the selected profiles and of assessing the sedimentation rate?

In order to discover indications of the trophic changes, oxygen conditions and emission of pollutants, the content of the main nutrients, some heavy metals and organic compounds were analyzed. Special attention is paid to chemical tracers specific to the local industrial effluents. Such tracers, with a known loading history, may provide valuable support for the evaluation of the radionuclide based dating of sediment profiles. The conclusions of the pollution history of Lake Vanajavesi are, however, mainly based on the biostratigraphic evidence. The integration of stratigraphic parameters is reported by Kansanen (1985).

2. Study area

Lake Vanajavesi forms a part of the southern drainage basin of the River Kokemäenjoki, southern Finland (roughly 61°N, 24°E, Fig. 1). The lake and the countryside surrounding Lake Vanajavesi are described in detail by Uotila (1971) and Kansanen & Aho (1981).

The bedrock of the area is mainly Precambrian micaceous gneisses. Granite and granodiorite are also found (Matisto 1970). There are only a few outcrops of bedrock. The length of the rocky shore of Lake Vanajavesi is only a few kilometres, including the islets.

The bedrock is covered with thick deposits of glacial till or outwash material in the the form of long eskers. The most essential feature is, however, the high abundance of glacial clays. In many places the waters are fringed by broad zones of clays. Silty clay is most abundant; heavy clay and silt are rather rare (Erviö 1965). The water level of Vanajavesi was lowered artificially in the 18th century (Palander 1767, Mellenius 1789) and again in 1857 (Palmén 1903, Simola 1903). The latter lowering was the more significant, causing a drop in the water level of 2 m.

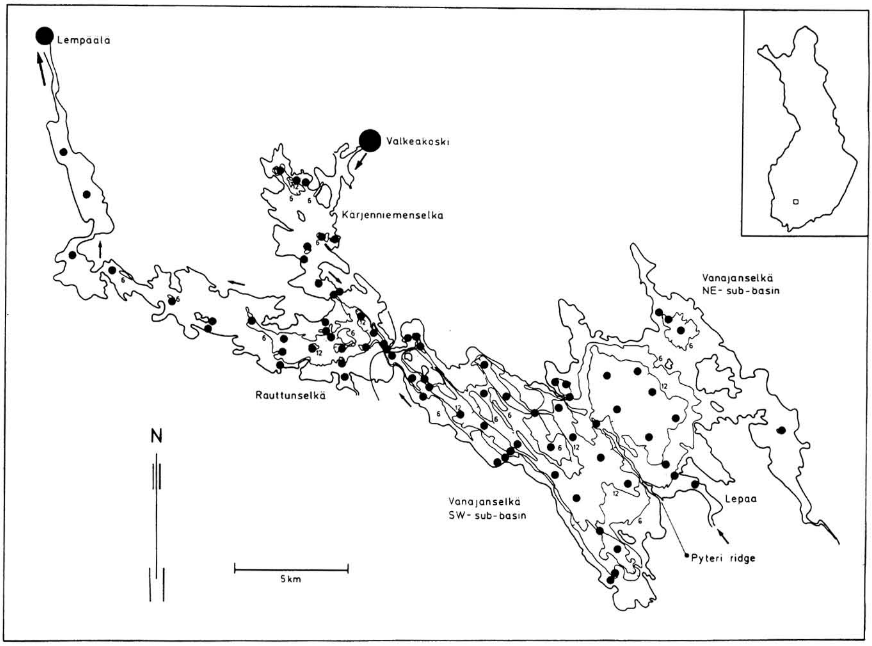


Fig. 2. The bathymetric map (contour lines of 6 and 12 m) of the study area. The location of the coring sites ($n = 79$) is indicated by black dots.

In both cases a broad zone of clayey alluvial material was exposed and a large amount of the surface material was washed back into the lake before the soil became bound by the invading vegetation (Vuorela 1980). The shoreline erosion of clayey material has been an important source of fine textured sediment.

The older postglacial history of Lake Vanajavesi was studied by Auer (1924) and Simola (1963). Vanajavesi was formed c. 8000 years ago, when land upheaval separated the lake basin from the sea at Lempäälä (see Fig. 2). The features of the lake basin have changed considerably since the separation, especially owing to the transgression induced by land upheaval, which was greatest in the northwestern part of the lake.

Lake Vanajavesi comprises several sub-basins (*selkä*-areas). The largest of those sub-basins which were included in the study area (Fig. 1) is Vanajanselkä. It has an area of 119.2 km^2, mean depth of 7.9 m, maximum depth of 24 m and mean volume of 936.7 × 10^6 m^3 (Kajosaari 1964). The theoretical retention time is 490 days. The bottom topography is rather complicated (Fig. 2). The basin is divided into two halves by the partially submerged Pyteri ridge, which prevents water exchange between the southwestern and northeastern sub-basin of Vanajanselkä. There are long and narrow bottom depressions in the NW-SE direction in the southwestern sub-basin. They stretch without any break to the basin of Rauttunselkä in the west. The northeastern sub-basin is bathymetrically more even. Vanajanselkä receives waters from the upper watercourse at Lepaa (Fig. 2), where the mean discharge is 19.4 m^3/s (Kajosaari 1964).

The other sub-basins to the west of Vanajanselkä are shallow flow-through basins typical of Finnish watercourses. Their mean depth varies between 1.6-4.8 m (max. depth 11-24 m) and the theoretical retention time is 4-25 days. The western basins receive waters from Vanajanselkä and from the northeastern watercourses of Längelmäki and Hauho at Valkeakoski (mean discharge 35 m^3/s).

Table 1. Mean values of oxygen concentration (mg/l), specific conductivity (mS/m +25°C), pH, total nitrogen (µg/l) and total phosphorus (µg/l) of the water at standard depths of 1, 5, 10 and 15 m, based on measurements made during March-April in 1970-1978 by the local water protection association and National Board of Waters. For references and exact location of the sampling stations, see Kansanen & Aho (1981).

	Depth m	Kärjen-niemen-selkä	Rauttun-selkä	Vanajan-selkä, SW	Vanajan-selkä, NE
O$_2$(mg/l)	1	4.6	9.5	10.3	11.2
	5	1.5	2.8	10.2	10.8
	10	0.3	0.5	4.8	8.5
	15	0.3	0.2	2.3	3.8
mS/m	1	13	15	14	14
	5	39	20	14	14
	10	55	21	16	14
	15	57	24	18	15
pH	1	6.3	6.7	6.8	6.9
	5	4.8	6.3	6.8	6.9
	10	4.3	6.2	6.5	6.7
	15	4.4	6.5	6.4	6.6
Total N	1	600	800	1300	1000
Total P	1	30	40	40	30

The whole study area is nowadays highly eutrophic and some parts are heavily polluted (e.g. Kansanen & Aho 1981). Algal blooms and hypolimnetic oxygen depletion are common phenomena in this previously more or less oligotrophic lake (Järnefelt 1929). The water colour is brownish due to humic materials typical of Finnish lakes (mesohumic). Some limnological background data is given in Table 1; for further details see Kansanen & Aho (1981).

The impact of man in the area surrounding Vanajavesi has been heavy over a long period of time. The area in fact belongs to the oldest agricultural region in Finland. Palaeoecological investigations have shown that the earliest clear signs of agricultural activities date from the Late Roman time (A.D. 200-400) and the Migration period (A.D. 400-600) (Tolonen, M. 1979). More important than agriculture have been the urban concentrations and industrial plants, due to their high waste water load.

The waste water loading is concentrated in two main regions. Hämeenlinna (Fig. 1) is the oldest and biggest urban centre with many small or middle scale industrial plants. The town was founded in 1638. Its municipal sewer network was taken into use in 1911, when the number of inhabitants was 6400. Today Hämeenlinnna has about 42 000 inhabitants. According to Oravainen (1983), the proportion of the Hämeenlinna region (in the wide sense) is at present about 9 %, 50 %, 43 % and 16 % of the total BOD_7, nitrogen, phosphorus and suspended solids loading directed at Lake Vanajavesi. The load thus consists mainly of nutrients, which have a fertilizing effect on Vanajanselkä.

The Valkeakoski industrial centre is the most important source of waste waters in the study area. About 90 %, 33 %, 46 % and 82 % of the total BOD_7, nitrogen, phosphorus and suspended solids load directed at Lake Vanajavesi come from Valkeakoski (Oravainen 1983). The first industrial plants were founded there in the second half of the 19th century: a wood-pulp mill and a paper mill in 1871, a sulphate pulp mill in 1880 and a sulphite pulp mill in 1907 (Autio & Nordberg 1972). A chemical rayon fibre factory started production there in 1943. The number of inhabitants of Valkeakoski in 1922 was 2800 and in 1981 23 000, persons.

Because the industry of Valkeakoski is the most important source of pollution, the production statistics of its products can provide a good picture of the relative increase of loading during the period 1871-1982 (Fig. 3). It was not possible to estimate the long-term changes in the total waste water loading discharged to Lake Vanajavesi as the older statistics were incomplete or lacking. It should be stressed, however, that the specific load per ton of product has decreased during the last years thanks to some improvements in industrial processes and waste water purification plants. The most important of these are the washing plant and the chemicals recovery plant of the sulphite pulp mill, which started up in 1975 and the lime precipitation and neutralization plant of the rayon fibre factory, which was taken into use in 1980. No increase in the total waste water load has taken place since 1975 (Table 2), when load statistics began to be reported on a regular basis.

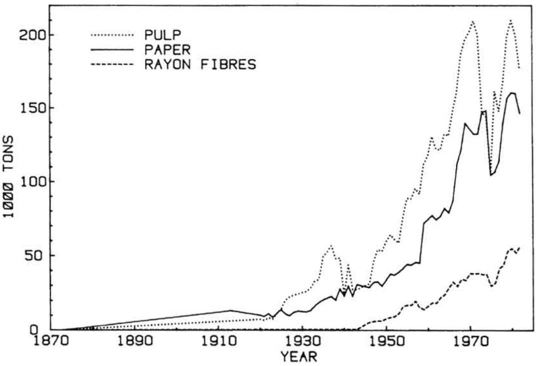


Fig. 3. The production of the main industrial products in Valkeakoski during the period 1871-1982 (10^6 kg/year).

Table 2. The measured total waste water load (kg/day) discharged to Lake Vanajavesi in the years 1975-1982 (Oravainen 1977, 1978 and 1983).

Year	BOD_7	Total-N	Total-P	Suspended solids
1975	34326	1450	125	
1976	29375	1255	88	
1977	24210	1516	84	14711
1978	24260	1601	93	13400
1979	29845	1538	105	15454
1980	30916	1665	101	14889
1981	29616	1808	117	15833
1982	25114	1616	98	10233

3. Material and methods

3.1. Field work

Sampling was started in the summer of 1979 by taking short profiles (length 13-36 cm) from the surficial sediments at 79 sampling sites, which were mainly the same ones used in the earlier zoobenthos studies of Kansanen (1981) and Kansanen & Aho (1981). The location of the sampling sites is presented in Fig. 2. Profiles were taken with a Kajak-type gravity corer (tube diameter 83 mm), which takes undisturbed samples even from the loose surficial layers (Hakala 1971). After lifting, the cores were described visually and the thickness of various sediment layers was measured with the sample still in the plexiplast tube. Each core was then subsampled by pushing it upward with a piston and cutting a 1 cm thick slice from standard depths using a slicing device (Hakala 1971) fitted to the upper end of the tube. The thickness of the slice was measured from a scale on the piston rod. The visual observations were checked during the slicing procedure. The thickness measurements of visible sediment layers are quite rough because the limits of most layers were more or less diffuse. The standard depths, from which sub-samples were collected as quantitatively as possible, were 0-1 cm and 19-20 cm, or in the case of very short cores 9-10 cm. All sub-samples were transferred to polyethylene bags and kept frozen until analyzed.

Following this first stage of sampling, four coring sites were selected for more detailed investigations (KS1, RS2, VS1 and VS3, Fig. 8). 35-36 cm long cores were taken at each site with the same Kajak corer for radiochemical dating and chemical analyses. Cores were cut on a boat, using the same device as earlier, into 1.0, 1.3 or 2.0 cm thick slices. Replicate cores were taken for resin acid and biostratigraphic analyses. When the cores for the biostratigraphic analyses were taken an additional lead weight was used in the Kajak corer. Thus, the length of these cores measured up to 50.5 cm. An attempt was made to take the cores at exactly the same place (calm weather, sampling point marked with a buoy). The visual stratigraphy of the replicates was compared and no deflections were noted.

Because the uppermost sediment at sampling site KS1 was laminated, a sediment block frozen *in situ* was obtained with the freezing device of Huttunen & Meriläinen (1978) from ice in the spring of 1981. The sample contained 26.5 cm of sediment below the undisturbed (sharp) sediment-water interface.

3.2. Physical and chemical analyses

Water content was measured by weight loss at 105°C after 6 hours. The organic content is expressed as loss-on-ignition, which was determined at 550°C (2 hours). The bulk density of the fresh sediment was determined according to the formula given by Axelsson & Håkanson (1971):

$$\rho = 100\rho_m / [100 + (W + IG')(\rho_m - 1)]$$

where ρ_m = the density of the inorganic material (g/cm^3), W = water content (% of wet sediment) and IG' = organic content (% of wet sediment).

The above equation is based on the assumption that the density of the water as well as the density of the organic matter is 1.0 g/m^3. The value of 2.65 g/cm^3 was used as ρ_m, which is generally applied in the grain-size analyses of clayey soils based on sedimentation (Elonen 1971). This value was checked from 9 randomly selected samples with a helium-air pycnometer and was found to be reliable. The bulk density calculations agreed well with the results obtained by direct volume-weight determinations.

In the particle size determinations of the sedimentary inorganic matter the organic matter and most of the inorganic impurities were removed by treating with H_2O_2 and HCl, as described by Elonen (1971). The sediment suspension was peptised with $Na_4P_2O_7$ and sieved through a sieve having a mesh size of 0.044 mm. Most samples penetrated this sieve almost completely. Those samples having larger amounts of coarser material were sieved through a standard series of sieves. The particle size distribution of the fine material was determined with a Sedigraph analyzer (Kemira Oy, Oulu Research Laboratory), which draws the settling curve automatically.

All sediment grain sizes (Φ) are given in phi units (phi = $-\log_2$ particle size diameter in mm) and distribution statistics expressed as mean, standard deviation, skewness and kurtosis are calculated according to Folk & Ward (1957):

mean $$M_z = [\Phi(16) + \Phi(50) + \Phi(84)] / 3$$

standard deviation

$$\sigma_I = [\Phi(84) + \Phi(16)] / 4 + [\Phi(95) + \Phi(5)] / 6.6$$

skewness

$$Sk_I = \frac{\Phi(16) + \Phi(84) - 2\Phi(50)}{2[\Phi(84) - \Phi(16)]} + \frac{\Phi(5) + \Phi(95) - 2\Phi(50)}{2[\Phi(95) - \Phi(5)]}$$

kurtosis $$K_G = \frac{\Phi(95) - \Phi(5)}{2.44[\Phi(75) - \Phi(25)]}$$

where Φ(5), Φ(16), Φ(25), Φ(50), Φ(75), Φ(84) and Φ(95) correspond to the phi diameter of these percentiles of the cumulative frequency curve. When the distribution curve drawn on the arithmetic probability paper and the phi scale remained open-ended at the fine end of the distribution, the straight line of the known part of the clay size area was continued further and the lacking percentiles were then read off the extrapolated curve (cf. Folk & Ward 1957).

Carbon was analyzed with the carbon analyzer and method developed by Salonen (1979). Total nitrogen was determined according to the Kjeldahl method. In the analysis of total phosphorus, samples were combusted with concentrated nitric and perchloric acid. The aliquot was analyzed with Technicon AutoAnalyzer (Kemira Oy, Espoo Research Centre) using the standard molybdenum-blue method.

For the metal determinations the samples were digested by successive treatments with HNO_3, $HNO_3 + HClO_4 + HF$ (1:1:8), $HClO_4$ and HCl. Zn, Al, Cu, Ni and Pb were analyzed using the AAS flame method. Cd was determined using flameless AAS (Kemira Oy, Oulu Research Laboratory). The extraction technique used gives good estimates of the total concentrations of metals in sediments (e.g. DeGroot et al. 1982).

The sedimentary chlorophyll derivatives were determined spectrophotometrically from acetone extract according to the method of Vallentyne (1955), modified by Sanger & Gorham (1972). Results were calculated as arbitrary units according to the following equation (cf. Simola 1983):

$$\text{units/g} = 10V(A_{667} - A_{750}) / (M \cdot IG \cdot L)$$

where A_n = absorbance at wavelength n (nm), V = extracted volume (ml), M = dry weight of the sample (g), IG = organic content (% of dry sediment) and L = cuvette length (cm). The arbitrary units are thus given per gram of organic matter in sediment.

For the resin acid analyses the frozen samples were smelted and their pH was set to 2-3 with 5% HCl. The samples were frozen again and placed in a freeze-drier (Hetosicc) for 24 h. About 5 g of homogenized sediment was extracted in an ultrasonic bath with 25 ml of methylene chloride (15 min). Resin acids were analyzed by gas chromatography using an internal standard method. Abietic acid (Fluka AG) was used as a standard and diphenylphtalate as an internal standard.

The resin acid analyses were carried out by a gas chromatograph Carlo Erba 2300 equipped with:

- — capillary column SE-54, 25 m, J&W Scientific Inc.
- — an FID detector
- — carrier gas HE, flow rate 2 ml/min
- — oven temperature programming 190°C for 5 min, heating 10°C/min to 250°C
- — an integrator, Hewlett Packard Lab Data System with an ISTD-program

A qualitative analysis of most of the samples was also carried out by a capillary column gas chromatograph-mass spectrometer system (Nermag S.N.A.) equipped with a SE-54 column.

3.3. Microscopic analysis of laminated sediment

The possible annual character of the laminations of the frozen core KS1 were checked by the procedure developed by Simola (1977). Adhesive tape peel preparations were made from the smoothed and dried vertical surface of the frozen sediment block. Diatoms were counted with a Leitz Dialux microscope at 600× magnification along the midline of the tapes in successive visual fields with a diameter of 0.345 mm.

Four replicate columns were sawn from the uppermost 13 cm of this flat sediment block for further analyses. Each of them was dissected into 13 subsamples along selected grey striae clearly visible in the black sediment. The vertical thickness of these subsamples was 0.6–1.2 cm, containing 1–3 varves.

The average dry matter accumulation rate (g/cm^2/year) was obtained for each subsample using the value of the linear accumulation rate (cm/year), measured values of water content and organic content (one replicate column was used for these determinations) and the estimated value of the fresh bulk density of the subsample from the formula given earlier.

3.4. Radiochemical dating

For dating sediment layers the distribution of the radionuclides ^{137}Cs, ^{239,240}Pu and ^{210}Pb in four sediment cores were determined.

^{137}Cs was determined gamma-spectrometrically directly from dried samples using NaI well crystal and a multichannel analyzer. In determinations of ^{137}Cs the main interference was due to the natural radioisotopes ^{214}Bi and ^{40}K. The results were corrected for these two radionuclides.

For determining ^{239,240}Pu the samples were wet ashed using a mixture of nitric acid and hydrochloric acid. Plutonium was separated by anion-exchange and electrodeposited on to a platinum or stainless steel disc. The ^{242}Pu isotope was used as a tracer for the calculation of the chemical yield. The alpha-activity was determined using a silicon surface-barrier semiconductor detector and a multichannel pulse height analyzer. The total amount of ^{239}Pu and ^{240}Pu isotopes are given since the difference between the alpha energies of these two isotopes is too small to be separated alpha-spectrometrically.

The content of the natural radionuclide ^{210}Pb in the samples was determined by measuring the daughter nuclide ^{210}Po, which was separated from the sediment samples (200–500 mg of dry weight) by leaching with the mixture of HNO_3 and HCl. ^{210}Po was deposited on a silver disc and the alpha activity was determined using the same detector system described above for plutonium. ^{209}Po was used as chemical tracer.

4. The areal distribution of the surficial sediments

When the pollution history of a lake is studied, conclusions cannot be based on one or two more or less randomly selected cores, not, at least, in large and complex water bodies such as Lake Vanajavesi. Data on lake bottom dynamics, i.e. where areas of erosion, transportation and accumulation appear, is important in selecting representative coring sites, where the deposition of fine materials has taken place continuously without any interruptions during the time period of interest (for definitions of these terms, see Håkanson 1977b, 1982). Mapping of the surficial deposits by taking short cores may give valuable information on bottom dynamic conditions in complex lake basins.

Analyses of specific pollutants from the surficial deposits can be used in mapping the geographical distribution of the waste waters of a certain source of pollution. This kind of horizontal reference material is also needed for selecting representative coring sites and for interpreting the vertical changes in time. Information on lake bottom dynamics is also needed for interpreting the geographical distribution of pollutants as the grain size essentially influences the absolute concentrations in sediments (Förstner & Wittmann 1979).

4.1. Localization of the accumulation bottoms

4.1.1. Sediment grain size and its significance

It has been shown that there is often a relationship between the prevalent water dynamics, bottom dynamics (erosion, transportation, accumulation) and the physical character of the bed deposits (see e.g. Hjulström 1935, Sundborg 1956, Norrman 1964, Sly 1978 and Håkanson 1982). The grain size of a clastic sediment is a measure of the energy of the depositing medium and the energy of the basin of deposition. In general, coarser sediments are found in higher-energy environments and finer sediments in low-energy environments. Nevertheless, an important limiting factor is the availability of grains of various sizes (Reineck & Singh 1980).

In practice the visible features in the stratigraphy of the sediment core, such as the occurrence of gravel and sand (coarse deposits) or e.g. glacial clay, can give hints of disturbances in the sedimentation at the given site. Conclusions of present erosion or sedimentation can also be drawn from echo-sounding diagrams of the bottom deposits (e.g. Kukkonen 1973, Kemp et al. 1976).

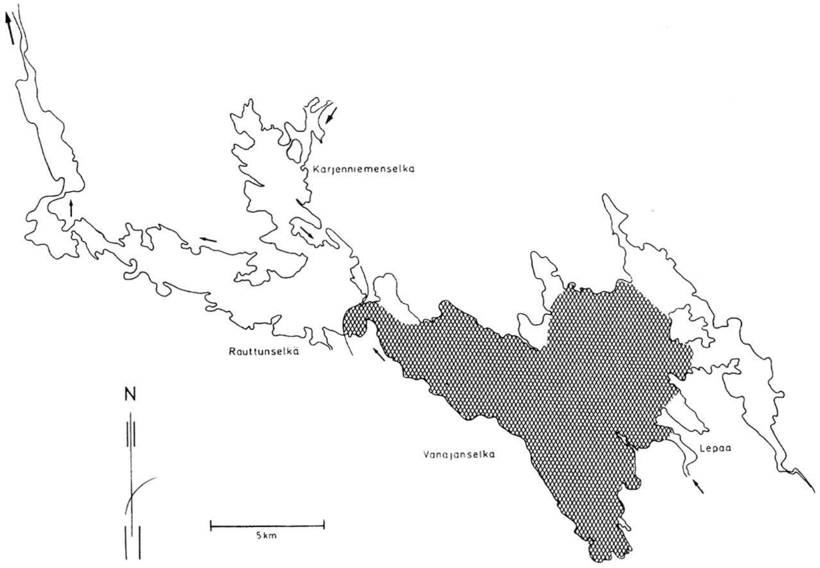


Fig. 4. The main basin of Vanajanselkä (shaded area). Other areas studied were defined as 'small basins'.

Regional variations in grain size may be helpful in the reconstruction of the basin of sedimentation, although the method has several limitations (Reineck & Singh 1980). Several authors have used grain size distribution parameters of the surficial sediments to deduce the integrated energy level at the site of deposition (e.g. Thomas et al. 1972, 1973, 1976, Damiani & Thomas 1974, Sly 1977 and Sly et al. 1982).

The best sorted materials correspond to sand-size particles requiring the least erosional velocity to induce motion (Sly 1978). Very fine particulates (clays) improve in sorting as a result of selective transport and deposition. Coarse fractions (gravels) also improve in sorting as a result of the selective winnowing of fine materials. According to Sly (1978), surficial sediments having equivalent size and sorting characteristics may be used, therefore, to show that the integrated dynamic energy levels to which they respond are in essence the same.

The aim of this part of the study is to test whether it is possible to establish a relationship between the measured grain size distribution parameters of the 78 surficial (0-1 cm) samples and the energy conditions in Lake Vanajavesi. If such relationships can be found, selected parameters are used in determining the accumulation areas suitable for representative coring. Water content and organic content are included in this analysis because both parameters have sometimes been used as key parameters indicating sedimentation conditions (e.g. Håkanson 1982, Hargrave & Kamp Nielsen 1977).

The minerogenic matter in the surficial sediments of the study area is characterized by fine grain size. This is partly due to the sampling, in which the littoral region, having always coarse sediments, was excluded (depths 2-23 m). When the particle sizes were graded according to the classification of Shepard (1954) (lower size limit for sand 0.063 mm and for silt 0.004 mm), 61 samples were clays, 12 silty clays, 2 sand+silt+clay and 3 clayey sands ($n=78$).

4.1.2. Measures of energy conditions

In order to verify the possible relationship between the measured physical sediment characteristics and the dynamic energy level only indirect and rough measures of energy can be used since direct measurements are lacking. The wind stress (in the form of waves, circulation, upwelling, coastal jets and seiches) is the most important factor affecting the processes of erosion and sedimentation in large lakes (Sly 1978). When the river plume areas, where river action is the dominant energy source, are eliminated it can be

Table 3. Linear correlation coefficient matrix for physical and chemical sediment parameters measured from 76 surficial (0-1 cm) sediment samples and for water depth at the sampling site.

	Depth	H_2O-%	Mean	Clay-%	*SD*	Skewness	Kurtosis	IG-%	Zn
H_2O-%	0.17								
Mean size Φ	−0.04	0.73***							
Clay-%	−0.05	0.75***	0.95***						
SD	0.17	−0.54***	−0.71***	−0.85***					
Skewness	0.33**	−0.47***	−0.75***	−0.68***	0.39***				
Kurtosis	0.00	0.22*	0.33**	0.35**	−0.28*	−0 .29**			
IG-%	−0.06	0.32**	0.16	0.31**	−0.37***	−0.07	0.08		
Zn	−0.18	0.20	0.11	0.27*	−0.45***	−0.09	0.01	0.77***	
Al	−0.41***	0.31**	0.53***	0.48***	−0.33**	−0.64***	0.16	−0.30**	−0.19

assumed that the general energy level decreases with increasing depth (Sly 1978). There are, however, several factors which modify the effect of wind (e.g. orientation, shape, size and surrounding relief of the lake basin, duration, speed and prevalent direction of wind and coriolis force). Because Lake Vanajavesi constitutes several sub-basins of different sizes, it is appropriate to divide them into two groups: the large Vanajanselkä and 'small basins'. The bays of Vanajanselkä, which are partly isolated from the main basin, are included in the latter group. Thus, the main open basin of Vanajanselkä (Fig. 4) has a total area of 99.3 km^2 and the maximum effective fetch at the sampling sites on average is 4.8 km (for calculation, see Beach Erosion Board 1972). 'Small basins' have a surface area of 1.2-27.8 km^2 and the maximum effective fetch at the sampling sites on average is 2.6 km. Depth is used in both groups as an indirect measure of energy.

In morphometrically complex lake basins the effect of bottom topography has to be taken into account. According to Håkanson (1977b), slopes of the bottom greater than 3.8 % clearly affected the sediment character in Lake Vänern. Steep slopes are often found in topographical bottlenecks, between islands, in bottom depressions, which can control water movement on a larger scale. Therefore an index of 'bottom roughness' may offer a better way of taking the bottom topography into account than the slope, which is very difficult to determine accurately for a given sampling site.

A simple index of bottom roughness was calculated from the sounding map (The National Board of Navigation, unpubl.). It was defined as the standard deviation of the water depths in a grid surrounding each sampling site (240×240 m, 24 depth measurements). This crude index describes well the topographic features in the surroundings of the sampling site. The bottom topography of the deep-water area is more even in the small basins than it is in Vanajanselkä (see Fig. 2). The values of the index varied between 0.2-4.3 (mean 1.3) at the sampling sites in the deep-water (9-24 m) area of the small basins. The corresponding figures for Vanajanselkä were 0.5-8.9 (mean 2.4).

4.1.3. Relationship between sediment parameters and water depth

If all samples taken from the study area are considered, there is in practice no linear correlation between the measured physical sediment parameters and water depth (Table 3). This may indicate that water depth is a poor measure of energy level in the study area, and/or that the relationship is not linear. The possible relationships are best examined using scatter plots and group 'small basins' as a test area because the effect of bottom topography there is probably less than in Vanajanselkä.

The scatter diagrams of six physical sediment parameters plotted against depth in small basins is presented in Fig. 5. According to Håkanson (1981b), who used the water content of the surficial sediment as a key parameter, the mean water content increases with lake water depth in areas where accumulation takes place in the deepwater area. The increase is not, however, linear, because there is a certain 'critical depth" below which the water content is quite constant (accumulation zone). Above this depth, where the processes of erosion, transportation and accumulation may all appear, the water content is very variable, though the general trend is towards lower values. In order to demonstrate whether such a trend can be seen in small basins, a logarithmic function $y = b(1) + b(2)\,e^{b(3)x}$ was fitted by the least squares method to this material. A "critical depth", which is a theoretical limit between the accumulation zone and transportation zone, was calculated from the ETA-diagram of Håkanson (1981a) usig the average value of the effective fetch (2.6 km) for small basins. This was done only for demonstrative purposes because such a limit is only a rough simplification of a complex issue.

Of the physical parameters, the standard deviation of the particle size distribution seems to follow the expected trend best (Fig. 5). It is almost constant in the deep-water area and tends to increase in the shallow-water region. The skewness appears to become negative in the shallow-water region and is almost 0 (normal distribution) in the deep-water area. In both cases dispersion is considerable in the shallow-water region.

Other parameters seem to be rather insensitive to the water depth. If some relationship exists, this is next to linear. Water content increases only very slightly with depth (linear $r = 0.47^{**}$). Mean particle size (in phi) which is correlated with water content ($r = 0.73^{***}$, Table 3), is not dependent on water depth (linear $r = 0.32$). The same can be said of kurtosis ($r = 0.35$). The organic content has considerable dispersal in relation to water depth.

The standard deviation of the particle size distribution is generally considered in geology as a coefficient of sorting, although according to Sly et al. (1982) it is a simplification. The standard deviation is strongly dependent on the mean particle size. In the material of this study the lowest values for the standard deviation (best sorting) are found in samples having the finest particle size (linear $r = -0.71^{***}$, Table 3). This is due to the fact that well-sorted sands were lacking in samples. Fig. 6 shows the relationship between standard deviation and skewness. Samples having the lowest standard deviation values have a skewness of around 0. When the standard deviation increases, the distributions tend to become slightly negatively skewed and at

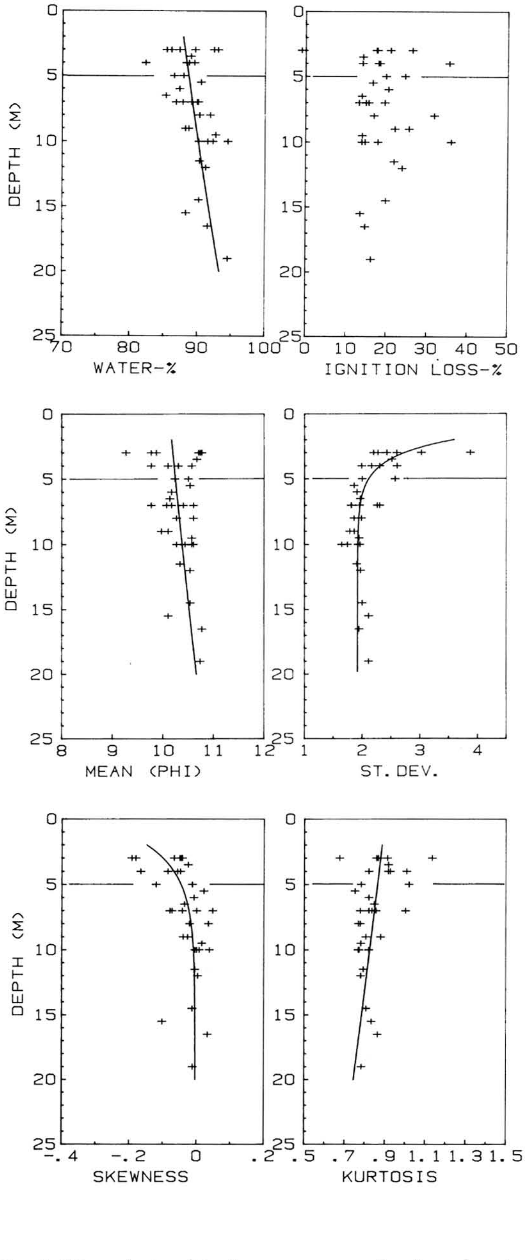
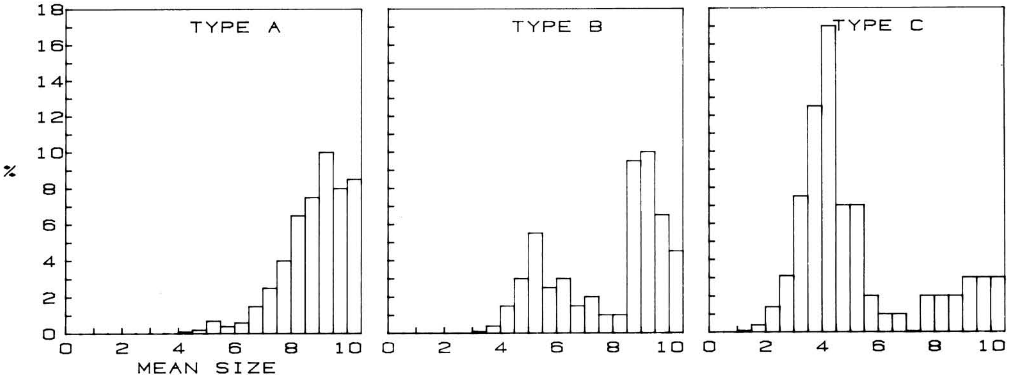


Fig. 5. The relationship between water depth and water content, organic content, mean particle size (in phi), standard deviation, skewness and kurtosis of the particle size distribution of the surficial sediments (0–1 cm) in the group 'small basins'. The critical depth (4.9 m) is indicated by a horizontal line (Håkanson 1981a). The logarithmic function $y = b(1) + b(2)\,e^{(b(3)\,x)}$ was fitted by the least squares method to demonstrate the general trend.



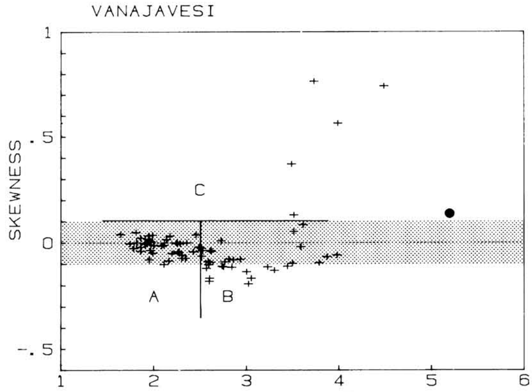


Fig. 6. The relationship between standard deviation and skewness of the particle size distribution of the surficial sediments in 78 cores (0–1 cm) (lower figure). The area of normal distribution for skewness is indicated by the shaded zone (cf. Folk & Ward 1957). Typical size-frequency distributions for three groups A–C delineated in the lower figure are presented in the upper figures. A black dot indicates that the sample contains an abundance of Fe-Mn concretions hampering the grain size analysis.

approximately 3.5 positively skewed through the normal distribution. One sample containing disturbing amounts of large Fe/Mn-nodules does not fit the general trend well.

In order to demonstrate the meaning of the observed trend, typical size-frequency distributions were selected for three arbitrarily defined groups (Fig. 6). Group C consists of all clearly positively skewed (over 0.1) samples. The limit between groups A and B was set at a standard deviation of 2.5. Typical distributions were selected by calculating an average distribution for each group and by taking that distribution having the most similar distribution parameters to this. It was noted that all size frequency distributions in group A represent unimodal, normally distributed clay. Types B and C are both bimodal. In type C the peak in the silt-size area is stronger than in the clay region. It can be stated that the standard deviation/skewness diagram in this case provides a useful way of describing the grain-size distribution types. It can also be said that of the single distribution parameters the standard deviation alone adequately describes the degree of sorting in Lake Vanajavesi. It is umambiguously increasing here as the proportion of coarser grain-sizes increases because samples of well-sorted sands are lacking. It is positively correlated with the proportion of material coarser than 8 phi (silt+sand, linear $r=0.85^{**}$).

In large Vanajanselkä the relationship between the physical sediment characteristics and water depth is more complicated than in small basins. There is in fact no relationship between water depth and standard deviation if all samples are taken into account (Fig. 7). If, however, all samples having bottom roughness index values of over 2.8 and those samples taken from the river plume area at Lepaa are eliminated, there is a significant linear correlation ($r=-0.71^{***}$) between them (Fig. 7). The relationship is different to that noted in small basins. Low standard deviation values are reached at greater depths (below 15 m) than in small basins. The result indicates high dynamic energy levels in general and complex hydrodynamic conditions in the area of Vanajanselkä.

4.1.4. Comparison between sediment parameters and visual stratigraphy of the cores

According to the visual observations the cores taken from the deep-water zone (below 9 m) were divided into three categories. In

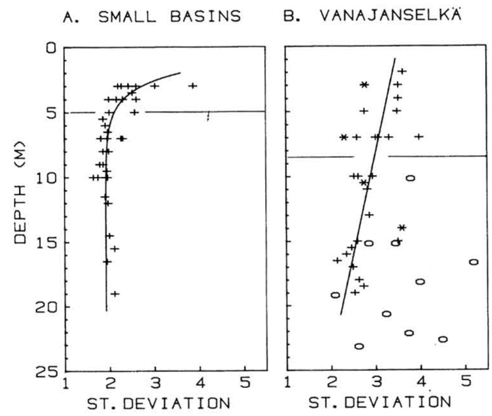


Fig. 7. The relationship between water depth and standard deviation of the particle size distribution of the surficial sediment (0-1 cm) in the group 'small basins' (Fig. A) and in Vanajanselkä. Samples taken from bottom depressions having a 'bottom roughness' of over 2.8 are indicated by a circle and samples representing the river plume area at Lepaa by an asterisk (Fig. B). The linear regression line in Fig. B is based on samples marked with a cross. Horizontal lines indicate the theoretical 'critical depth' (Håkanson 1981a).

Table 4. The distribution of bottom roughness index and physical sediment parameters (0-1 cm) in different profile types (mean ± *SD*). The *F*-statistic (the ratio of the among-type to the within-type variance of the values) has been presented as a measure of the degree to which the core types are defined by each variable.

	Type a *n*=31	Type i *n*=4	Type e *n*=9	*F* (2.41 *df*)
Bottom roughness	1.4±1.0	2.5±1.9	4.6±2.8	14.8***
Water content	90.0±2.0	88.2±1.4	85.6±6.4	6.2**
Organic content	17.2±4.6	16.5±2.1	16.6±1.5	0.1
Mean size Φ	10.7±0.3	10.0±0.5	8.4±2.5	13.5***
SD Φ	2.3±0.4	3.0±0.7	3.7±0.8	28.9***
Skewness	0.0±0.05	−0.1±0.05	0.2±0.4	6.6**
Kurtosis	0.8±0.1	0.8±0.1	0.8±0.2	1.3

profile type a (a refers to accumulation) all layers were very fine-textured clayey deposits. The uppermost 14-30 cm was black or blackish brown (or grey) FeS-coloured sediment. Below this layer the colour changed to light brown or grey. All layers were more or less homogenous, with the exception of three cores taken from Kärjenniemenselkä, where the black uppermost layer was clearly laminated.

In profile type e (erosion) there were visible layers of coarse sediment (sand) or old consolidated clays (greyish blue) at the base of the core. In a few cases there were also Fe-Mn concretions in these cores. This combination has been considered as an indication of the conditions under which sedimentation does not take place (Kukkonen 1973, Thomas et al. 1972, 1973).

Some cores were difficult to classify into these two types. Clear signs of disturbance in sedimentation were lacking. On the other hand the FeS-coloured layer was absent or irregularly stratified. These cores were classified into profile type i (indifferent). The bottom roughness and measured physical sediment parameters of three core types are compared in Table 4. The bottom topography largely determines the occurrence of clearly disturbed profiles in the deep-water area. All cores of type e and two of type i were taken from the morphometrically complex SW-subbasin of Vanajanselkä (cf. Fig. 2). Two cores of type i were taken from the river plume area at Lepaa.

The water content and organic content of the uppermost centimetre of the core have very little value in predicting the core type (Table 4). Of the grain-size distribution parameters the most useful is the standard deviation. There is little variation in the mean grain-size between the core types. Even in those cores in which there was compact glacial clay at the base and coarse sand above this, the mean size of the surficial centimetre was small because of fine clayey deposits on the surface of the sediment. This indicates that these bottoms are transportation areas where fine materials are transported by currents into accumulation areas having a low energy level, which makes the stable redeposition and accumulation of the fine clay possible (cf. Sly 1978, Reineck & Singh 1980).

4.1.5. Bottom dynamic map of Vanajavesi

The results presented above can be summarized in the form of a bottom dynamic map in which the main areas of accumulation of well-sorted fine clay are roughly delineated (Fig. 8). Only the deep-water region is considered because the situation is complicated in the shallow-water area. The criteria used in the delineation were: 1) The core should belong to core type a or i. 2) The grain-size distribution of the uppermost centimetre

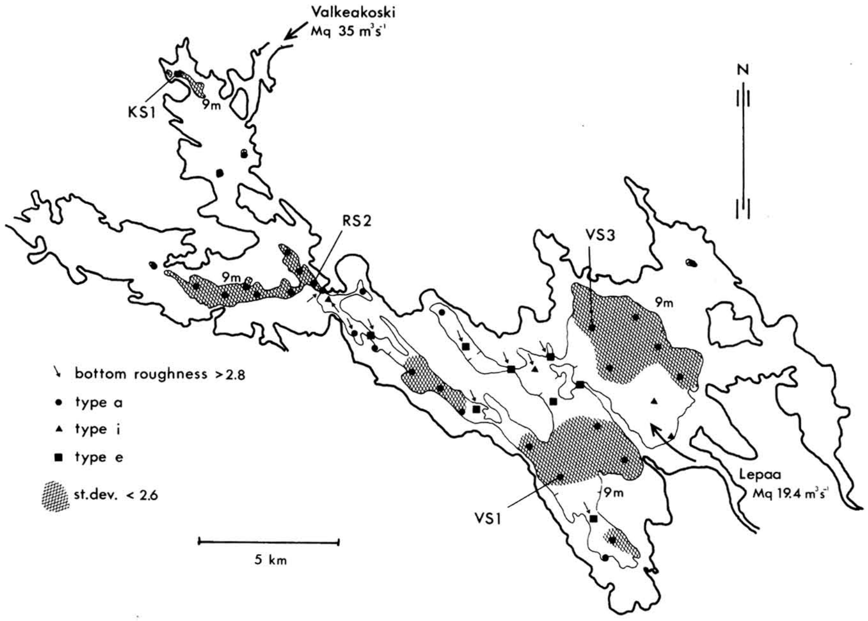


Fig. 8. Bottom dynamic map of the study area below a depth of 9 m. Types a, i and e refer to sediment core types (see text). Mq = mean discharge.

should represent unimodal well-sorted clay ($SD < 2.6$, cf. Fig. 6).

This kind of combination is suggestive of a low-energy environment, where the prequisites for undisturbed accumulation are best. It must, however, be pointed out that continous accumulation may take place even outside these areas. A relatively large bottom area in front of Lepaa is, for example, affected by high sedimentation due to the river plume effect (Fig. 8). Deflections of the grain size distribution there are due to the coarse materials transported by river currents.

4.2. Zinc in the surficial sediments

Some earlier authors have reported on elevated zinc concentrations in the surficial sediments of Lake Vanajavesi (e.g. Helsingin yliopiston limnologian laitos 1979, Koivo & Oravainen 1982, 1983). These high concentrations have been shown to be due to the effluents of the rayon fibre factory in Valkeakoski. The estimated and measured zinc load during the period 1943–1982 is presented in Fig. 9. Before the year 1980 the zinc load was high (even over 1000 kg/d). The effluents were at that time acid (pH 2–3). Recovery of Zn and neutralization were started in 1980, when the load dropped to a level of about 100 kg/d. Although zinc is a common pollutant in both industrial and municipal waste waters in general, for instance due to pipeline corrosion, other sources are in this case very small.

Until 1975 the zinc containing effluents were discharged into Lake Mallasvesi, just upstream of Vanajavesi. At present they load Kärjenniemenselkä directly. Most of the zinc is in a soluble ionic form when it is conducted into the lake. The effluents are rapidly mixed in the northern part of Kärjenniemenselkä with the waste waters of the wood-processing industry and the settlement. It is known that zinc has a strong sorption affinity. It is rapidly adsorbed by suspended particulate matter

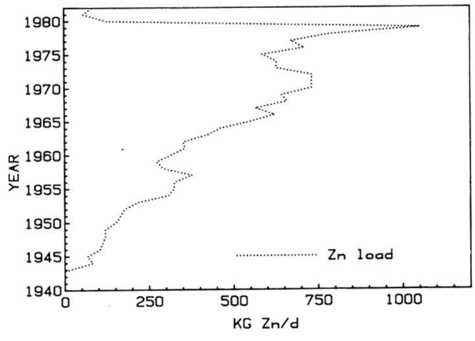


Fig. 9. Estimated (years 1943–1972) and measured (1973–1982) zinc load (kg/d) from the rayon fibre factory in Valkeakoski.

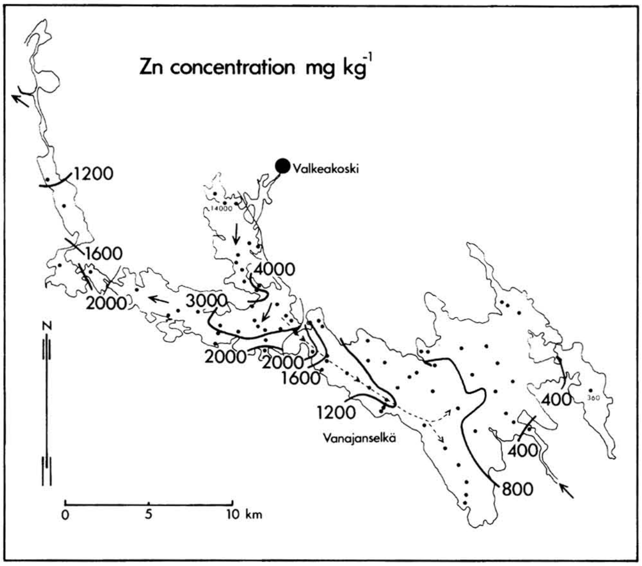


Fig. 10. The zinc content (mg/kg in dry sediment) of the surficial sediments (0–1 cm) in 79 sediment cores (black dots). The direction of the water flow is indicated by arrows. Direction of the waste-water flow during wintertime is marked with a dotted line. Max. and min. concentrations are indicated by small figures.

(both organic and inorganic, e.g. clay particulates) and it sedimentates with them quite rapidly from the water column (cf. Groth 1971, Nienke & Lee 1982). It is also known that resorption and thus remobilization of sedimented zinc can take place at a low pH (less than 6, Nienke & Lee 1982). Such acid conditions have prevailed in the hypolimnion of Kärjenniemenselkä due to the acid effluents (cf. Table 1).

It was suggested that zinc could be used as a tracer giving 'the fingerprints' of the total waste-water load from the Valkeakoski area. Pasternak (1974) studied the accumulation of heavy metals in sediments as an indicator of their dispersal by water courses from zinc and lead mining industries in Poland. Zinc showed the greatest degree of migration with the waste waters and its concentration in the sediments was approximately a function of the distance from the source of pollution.

Zn was analyzed from the 79 surficial sediment cores. The grain size effect always has to be taken into account when heavy metal concentrations of sediments are being compared (e.g. Förstner & Wittman 1979, DeGroot et al. 1982). Bruland et al. (1974) and Kemp et al. (1976) eliminated the effect by relating the heavy metal concentration to aluminum concentration. Aluminum was considered a "conservative element" having a uniform flux to the sediments from the crustal rock sources. It showed strong positive relationship to clay-% and is thus indicative of the clay mineral content (Kemp et al. 1976).

Aluminum also shows a positive correlation to the clay-% in Lake Vanajavesi, but the relationship is quite weak (Table 3). The aluminum content is rather constant in surficial sediments (mean 7.3 %, standard deviation 0.6, range 5.6–9.4 %, $n = 79$). This is due to the small variation in the sedimentary minerogenic matter. Hence, the aluminum correction did not change the general picture of the distribution of zinc in the surficial sediments of Lake Vanajavesi (linear $r = 0.99$ between corrected and uncorrected concentrations). Zinc is strongly positively correlated with the organic matter content (Table 3) (cf. Kemp et al. 1976, Håkanson 1977a).

The surficial concentrations indicate that zinc-containing waste waters have spread out from Valkeakoski in two main directions (Fig. 10). The natural main flow is downstream to the west, where the concentrations gradually decrease as a function of the distance from the source of pollution. The map clearly shows that these waste waters have also spread to the east, i.e. towards the main flow. The concentrations are high in the western part of Vanajanselkä and they gradually decrease to the east. The concentration isoplets conform well to the bottom topography of Vanajanselkä. They indicate that the waste waters have penetrated into Vanajanselkä in the long and narrow bottom depression of the southwestern sub-basin (cf. Fig. 2). The concentrations are clearly lower in the northeastern sub-basin than on the western side of the Pyteri ridge (Fig. 2, 10).

The range of concentrations in the uppermost centimetre is very wide, i.e. 360-14 000 ppm. In the lower part of the cores (19-20 cm or 9-10 cm) the range is 140-1600 ppm. This demonstrates that these depths do not represent a natural background level at all places. The lowest surficial concentrations were found in Lusinselkä and in the eastern part of Vanajanselkä at Lepaa (river plume area). This proves that the waste waters coming from the upper course in the Hämeenlinna region are not contaminated by zinc.

The observed distribution pattern of zinc agrees well with earlier observations on the waste waters based on water-chemical analyses (oxygen, conductivity, COD, lignin; see e.g. Ryhänen 1962, Rautalahti-Miettinen 1977). The penetration of waste waters from the Valkeakoski area upstream into Vanajanselkä was first noted in 1957 (Ryhänen 1962). It has been taking place during the wintertime, when, having a high specific density, the waste liquour follows the slope of the bottom. The extent of this phenomenon has varied greatly from year to year. Since the winter of 1979-80 it has been artificially inhibited by using aerators in the narrow strait between Rauttunselkä and Vanajanselkä with a good measure of success.

4.3. Selection of representative coring sites

Four coring sites were selected for more detailed investigations on the basis of the bottom dynamic map (Fig. 8) and the areal distribution of zinc (Fig. 10). Zinc analysis showed that selected coring sites had a different degree of contamination by the effluents of the main source of pollution. The surficial concentrations for Kärjenniemenselkä (profile KS1) were over 4000, for Rauttunselkä (RS2) over 3000, for the SW-sub-basin of Vanajanselkä (VS1) over 1000 and for the NE sub-basin (VS3) about 800 ppm Zn d.m.

5. Stratigraphy of the selected profiles

5.1. General description

5.1.1. Profile KS1

Site KS1 is located in the northern bottom depression of Kärjenniemenselkä (Fig. 8). Since the 1950s the basin of Kärjenniemenselkä has been heavily polluted by the waste waters of Valkeakoski (Ryhänen 1962). The water depth at the coring site was 10 m. At those depths water is usually permanently deoxygenated during the stagnation periods (Table 1). The pH has been low due to the acid effluents. In fact, the hypolimnion of the basin is poorly diluted waste water, which prevents natural vertical water circulation. Therefore, the basin is sharply thermally stratified in contrast to the other basins of Vanajavesi, where the stratification is labil (Kansanen & Aho 1981).

The uppermost 11.5 cm of the profile was clearly laminated, black in colour (FeS) and smelly sediment (Figs. 11 and 21). At a depth of 9.3-10.2 cm there was a grey clayey zone in the frozen sample. From 11.5 to about 27 cm the sediment was blackish grey and more homogenous than the uppermost layers. The laminations at that depth were more irregular and diffuse. Grey clayey homogenous sediment was reached at approximately 27 cm (± 1 cm). This general stratigraphy was common to all three cores taken from the deepwater area of Kärjenniemenselkä. The thickness of the clearly laminated layer varied between 11.5-16 cm. The grey clayey zone within this layer was observed in another core at a depth of 10-13 cm.

The stratigraphy of the water content, organic content, total carbon, total nitrogen, carbon-nitrogen ratio and total phosphorus is shown in Fig. 11. Vertical changes in organic content, total carbon, nitrogen and phosphorus are in principle similar. The minimum values are found in the lowest part of the core. There is a slight, and even, increase up to 12 cm and a sharp increase in the uppermost laminated part of the profile. The C-to-N ratio is lowest at the base of the core and has a tendency to increase towards the sediment surface.

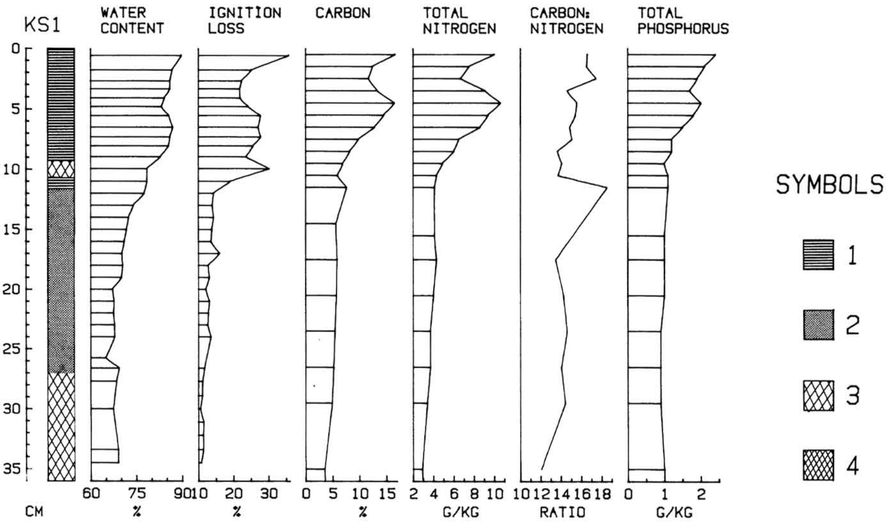


Fig. 11. Profile KS1. Water content of fresh sediment and some properties of dry sediment. Symbols for the lithostratigraphy used in the present study are: 1. black laminated sulphide clay-gyttja, 2. black or dark grey clay-gyttja with sulphide layers, 3. grey homogenous clay-gyttja, 4. brown homogenous clay-gyttja.

5.1.2. Profile RS2

Site RS2 is located in the eastern part of Rauttunselkä, which receives the polluted waters from Kärjenniemenselkä (Fig. 8). Thus, the water quality was poor in the 1970s (Table 1). The water depth at the coring site was 19 m. At this depth an oxygen deficit has been a common phenomenon, especially during winter. The pH has been markedly higher than in Kärjenniemenselkä. This is due to the greater degree of dilution of the waste waters.

The uppermost 25-27 cm of the profile consisted of a blackish-brown, homogenous FeS-sediment. Below this layer the sediment turned to grey and at approximately 34 cm to greyish-brown (Fig. 12). The thickness of the FeS-coloured layer varied in other cores taken from the deep-water area of Rauttunselkä ($n = 10$) between 20-28 cm.

The stratigraphy of the organic content is the reverse of that of site KS1. The highest values (over 20 %) are found in the lower part of the core. In the uppermost 25 cm the organic content is almost constant (15-17 %). The total carbon follows the trend observed in the organic content. The total nitrogen concentration has two peaks, one at the base of the core and the other at a depth of 4-5 cm. It increases markedly towards the sediment surface in the layer 26-4 cm. The carbon-to-nitrogen ratio decreases steadily from base to surface.

The total phosphorus stratigraphy is also different to that of core KS1. The highest values (over 2.4 g/kg) are found at a depth of 26-27 cm. From this peak the concentrations decrease towards both the base and the surface. There is, however, a slight increase in the uppermost 12 cm towards the sediment surface. The surface concentration of phosphorus is 1.9 g/kg.

5.1.3. Profile VS1

Site VS1 is located in the southwestern subbasin of Vanajanselkä (Fig. 8). The zinc concentration in the surficial cm is 1000 mg/kg (Fig. 10). The effects of the industrial waste waters in this area have been apparent during many winters (oxygen depletion in the hypolimnion, Table 1). The water quality is, however, discernibly better than in Kärjenniemenselkä or Rauttunselkä. The water depth at the coring site was 19 m.

The thickness of the blackish-brown FeS-sediment was 15-16 cm (Fig. 13). Below this layer the sediment turned to dark brown and at 30-31 cm to grey. This lithostratigraphy was

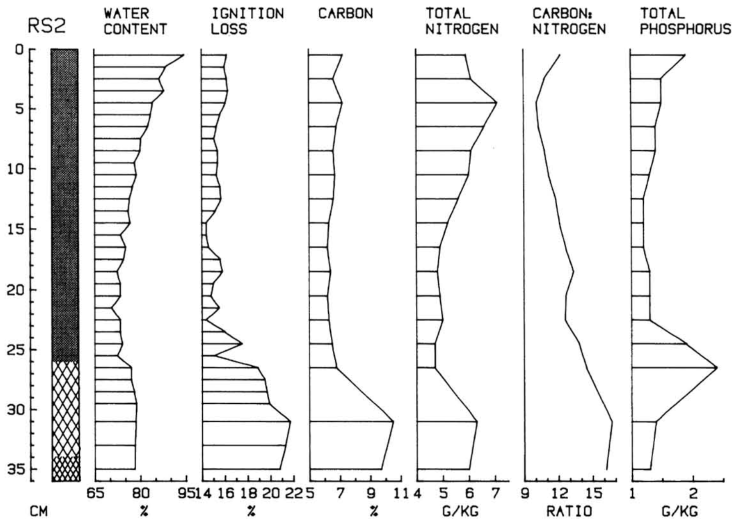


Fig. 12. Profile RS2. Water content of fresh sediment and some properties of dry sediment. For lithostratigraphic symbols see Fig. 11.

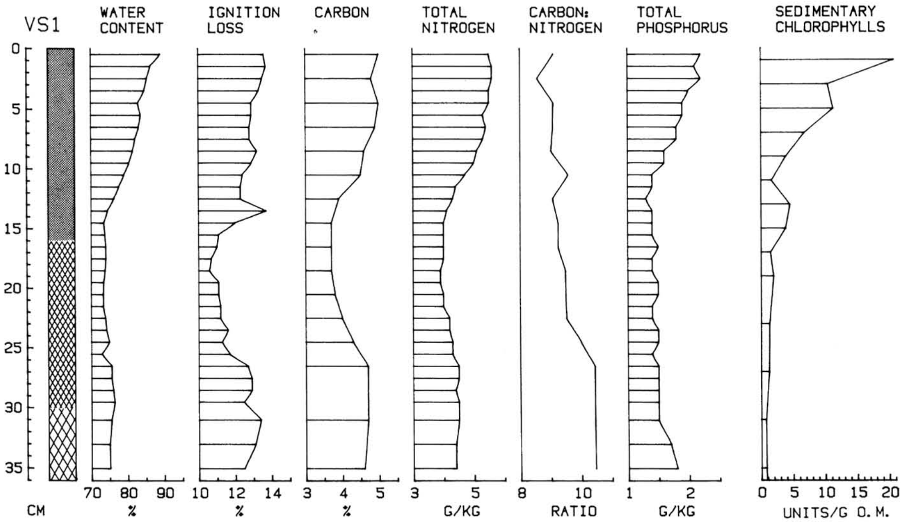


Fig. 13. Profile VS1. Water content of fresh sediment and some properties of dry sediment. For lithostratigraphic symbols see Fig. 11.

similar in the other three cores taken from this depositional basin (cf. Fig. 8). The thickness of the FeS-layer varied in these cores between 26–29 cm, hence was greater than at site VS1.

The stratigraphy of organic content and nutrient elements all follow the same general pattern. High values are found both at the base of the core and in the surficial layers. In the middle layers the concentrations are low (Fig. 13). The total nitrogen concentration clearly increases towards the sediment surface and the carbon-to-nitrogen ratio steadily decreases, as in core RS2. Total phosphorus shows some enrichment in the uppermost 12 cm.

In the sedimentary chlorophyll concentration the vertical changes are striking. The low concentrations (1 unit/g of organic matter) at the base of the profile increase slightly up to 17 cm, from which depth they sharply increase up to 20 units at the surface of the core.

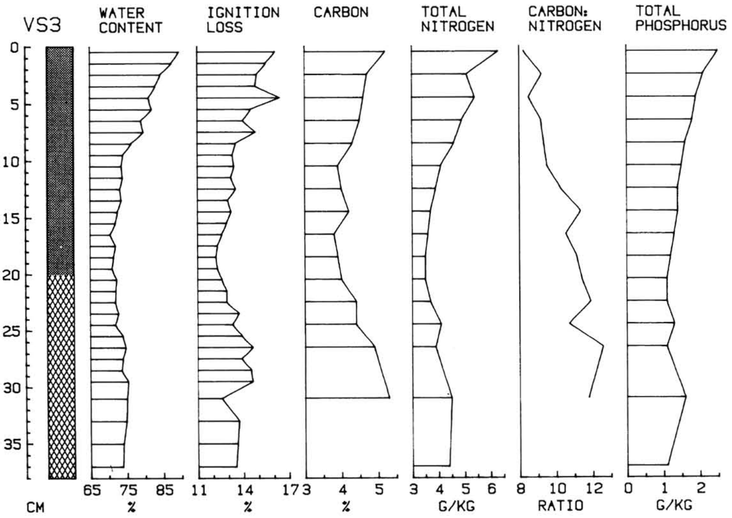


Fig. 14. Profile VS3. Water content of fresh sediment and some properties of dry sediment. For lithostratigraphic symbols see Fig. 11.

5.1.4. Profile VS3

Profile VS3 was taken from the northeastern sub-basin of Vanajanselkä (Fig. 8). No direct effects due to the waste waters of the Valkeakoski area have as a rule been detected here. The surficial zinc concentration is, however, clearly elevated from the background level up to 730 ppm. The production level has been raised by the nutrient rich waters coming from the Hämeenlinna area. The water quality of the NE-sub-basin has been slightly better during winter than in the southwestern sub-basin (Table 1). The water depth at the coring site was 20.5 m.

The visual stratigraphy corresponds to that of site VS1. The thickness of the dark grey layer (FeS) was 20 cm (in other cores within this accumulation basin 24–30 cm). Below the black layer the sediment was brown clayey mud (Fig. 14).

The stratigraphy of the nutrient elements and organic matter is similar to that of profile VS1. The vertical decrease in the C-to-N ratio is obvious. The total phosphorus increases steadily, especially in the uppermost 20 cm, towards the sediment surface. The organic content and total carbon have high values both at the base of the core and in the surficial layer.

5.1.5. Interpretation of the analyses

The palaeolimnological 'routine' analyses used in the general description of the profiles indicate, or at least give hints, of former oxygen conditions, production and nutrient status and the origin of the organic matter in sediments.

The blackish colour of the uppermost sediment layers in all cores is known to be due to the precipitation of sulphides during periods of oxygen lack in eutrophicated lakes (e.g. Digerfeldt 1972, Alhonen 1979, Tolonen 1980a). If the oxygen is completely consumed and the hypolimnion remains anoxic throughout the year, the sediment is black FeS-gyttja (Kärjenniemenselkä). If the oxygen depletion is restricted to shorter periods during stagnation, sulphide-bearing layers are formed within the brownish or greyish sediment column. The occurrence of blackish FeS-gyttja is therefore a simple and crude measure of oxygen status in the study area. All profiles clearly indicate deterioration in the hypolimnetic oxygen conditions during the latest stage of the lake development.

A linear correlation matrix for water content, ignition loss, carbon, nitrogen, phosphorus and some heavy metals and sediment depth in the profile is given in Table 5. The water content shows the highest cor-

Table 5. Linear correlation coefficient matrix for water content, ignition loss, total carbon, total nitrogen, total phosphorus, zinc, cadmium, aluminum and sediment depth (cm) in the profiles ($n=47$).

	H_2O-%	IG-%	C	N	P	Zn	Cd	Al
IG-%	0.34*							
C	0.33*	0.89***						
N	0.77***	0.64***	0.73***					
P	0.64***	0.19	0.00	0.34*				
Zn	0.61***	0.31*	0.46**	0.74***	0.01			
Cd	0.46**	0.27	0.37**	0.62***	0.07	0.68***		
Al	-0.60***	−0.77***	−0.80***	−0.79***	−0.34*	−0.51***	−0.31	
Sediment depth	−0.68***	0.06	0.14	−0.44**	−0.39**	−0.58***	−0.56***	0.09

relation with sediment depth (negative). The marked decrease in the water content is due to the compaction of the sediment. More interesting are the relationships between the organic content and nutrient elements (C, N, P). Both the total carbon and total nitrogen are highly correlated with the organic content. This is due to the fact that in acidic waters like Vanajavesi the precipitation of carbonates is negligible and therefore probably all the carbon is in an organic form. On the other hand, most of the sedimentary nitrogen is either also in an organic form or is adsorbed to organic matter (e.g. Ohle 1938). In contrast, the total phosphorus is not correlated with either the organic content or with carbon and the correlation with total nitrogen is weak.

Increases in the content of sedimentary organic matter can be due to the elevation in the level of primary production in the lake and/or increased inputs of allochthonous organic matter to the lake, provided that the input of minerogenic matter to sediments remains constant. The intensity of bacterial decomposition at the sediment surface affects the organic content, too (Digerfeldt 1972, Kukkonen 1973). Thus, the interpretation of the general trends seen in the profiles may easily be erroneous. The carbon-to-nitrogen ratio is a widely used index characterizing the origin of the organic matter (e.g. Hansen 1961). High values are typical of allochthonous sediments (dy). Organic matter produced by phytoplankton has a markedly lower C-to-N ratio (gyttja-sediments). The limit value between dy and gyttja sediments was set by Hansen (1961) at 10.

There is a similar decreasing trend in the C-to-N ratio towards the sediment surface in profiles RS2, VS1 and VS3. The trend is reversed in profile KS1. If the values at the base of each core (grey clayey layer) are compared, it can be seen that the ratio varies between 10.5-12 in profiles KS1, VS1 and VS3, but is obviously higher in RS2 (about 16). The lowest ratio in the topmost 5 cm varies between 8.5-10 in profiles RS2, VS1 and VS3, but is over 15 in profile KS1. The results indicate that allochthonous organic matter (humic substances) have been dominant in the pre-industrial layers (time scale given later) in all profiles. The highest allochthonous input can be seen in profile RS2. This is also indicated by high values for the organic matter content at the base of the core (over 21%). In other profiles the organic matter maximum at the base of the core varied between 11-14.5%. The abrupt changes in RS2 between 22-35 cm (IG, C, N and P) indicate possible disturbances in the normal sedimentation at this site.

The vertical decrease in the C-to-N ratio towards the sediment surface is a clear indication of the elevation of the organic production in the lake. This is supported by the stratigraphy of sedimentary chlorophyll derivatives. They have been used as indicators of the trophic status by e.g. Vallentyne (1955), Fogg & Belcher (1961), Sanger & Gorham (1972), Gorham et al. (1974). The rise in the concentration of chlorophyll derivatives is closely related to the increase in the organic production. It should be noted, however, that the anaerobic conditions favour the preservation of sedimentary chlorophylls in sediments (Gorham et al. 1974). Therefore, the very sharp, almost exponential, rise in the level of sedimentary chlorophylls in the uppermost 10 cm of profile VS1 can be partly due to the development of anoxic conditions during stagnation periods. These conditions are closely correlated with the eutrophication process.

There are several possible explanations for the trends observed in the organic matter and carbon stratigraphy of profiles VS1 and VS3. The increase towards the sediment surface within the FeS-coloured layer can easily be interpreted as an indication of the elevation of the production level. The radiochemical analyses at these sites did not show any abrupt changes in the sedimentation rate in the uppermost 20-25 cm. It is therefore probable that mineral sediment accumulation has occurred constantly in this particular case. Why are the values of the organic content so obviously higher at the base of the cores than in the middle part? If it is assumed that the allochthonous humus input and the dilution caused by minerogenic matter have remained constant, the vertical decrease up to the level at which the sediment turns blackish can be due to the increased intensity of the microbial activity. The increased nutrient inputs during the first phase have furthered the decomposition of humus by bacteria (cf. Ryhänen 1968, Kukkonen 1973). At a later stage the increased production of the lake itself has again caused the trend to alter towards higher organic accumulation. Another explanation for the high organic matter content at the base of the cores is that it is due to the artificial lowering of the water level in the middle of the 19th century (cf. p. 15). This possibility is discussed by Kansanen (1985).

The natural explanation for the inverse trend in the C-to-N stratigraphy of profile KS1 is the reception by Kärjenniemenselkä of the organic waste water load. Most of the sedimented organic material is of industrial origin and thus has a high C-to-N ratio. The production level of Kärjenniemenselkä has been lower than elsewhere in the study area (e.g. Salonen 1971). The increased waste water loading has therefore directly increased the content of organic matter and carbon from the base up to the surface in profile KS1. The abrupt increase at the level where the sediment becomes laminated can be due to the rapid increase in waste water loading (cf. Fig. 3). It is also possible that the influx of minerogenic matter decreased, or the decomposition of organic matter decreased, when the hypolimnion became permanently anoxic (cf. meromictic lakes).

The phosphorus content would appear to be a poor indicator of eutrophication in the cores examined. A feature common to all profiles is that phosphorus content increases from a level of 1.0-1.5 g/kg (at the base of the FeS-coloured layer) to about 2 g/kg at the sediment surface. This kind of phosphorus enrichment in the uppermost sediment layers of eutrophicated lakes has been reported by several authors (e.g. Kemp et al. 1976, Williams et al. 1976, Simola 1983). Under reducing conditions phosphorus may reprecipitate as vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and remain in the sediments (Rosenquist 1970). The slightly higher phosphorus concentrations at the base of profiles VS1 and VS3 compared to their middle part may be due to the fact that humus is able to stabilize phosphorus in the form of humus-iron complexes (Ohle 1963, Kukkonen 1973).

5.2. Heavy metals

5.2.1. Aluminum

Aluminum is one of the major elements in the sediment matrix. Concentrations varied between 5.2-8.5 % in four profiles (Fig. 15). Allan & Brunskill (1977) reported an Al content of 4.1-10.1 % from the clayey bottom sediments of Lake Winnipeg, Canada (total metal content). Aluminum shows a strong negative correlation with organic content, carbon and nitrogen (Table 5). Aluminum is mainly bound to the minerogenic matter of sediment. Thus, in order to eliminate the dilution caused by organic matter the concentrations are also calculated as a percentage of the ignited weight of the sediment.

Because aluminum is indicative of the clay mineral content of the sediment, a stable concentration of this element in the profiles indicates that the composition of the minerogenic component has remained constant. Aluminum has been used as an erosion indicator (e.g. Tolonen & Jaakkola 1983). It can be seen that aluminum shows very little variation in cores RS2, VS1 and VS3. In profile KS1 there is a sharp decrease in the uppermost 10 cm which is not due to dilution by organic matter. The reason is probably the low pH (even below 3) in Kärjenniemenselkä during the 1960s and 1970s. It has been demonstrated that a drop in the pH of the water greatly accelerates the passage of Al into solution. The critical pH is 5.0 (Tolonen & Jaakkola 1983 and references therein). The sharp peak in the aluminum content at 10 cm (grey clayey layer

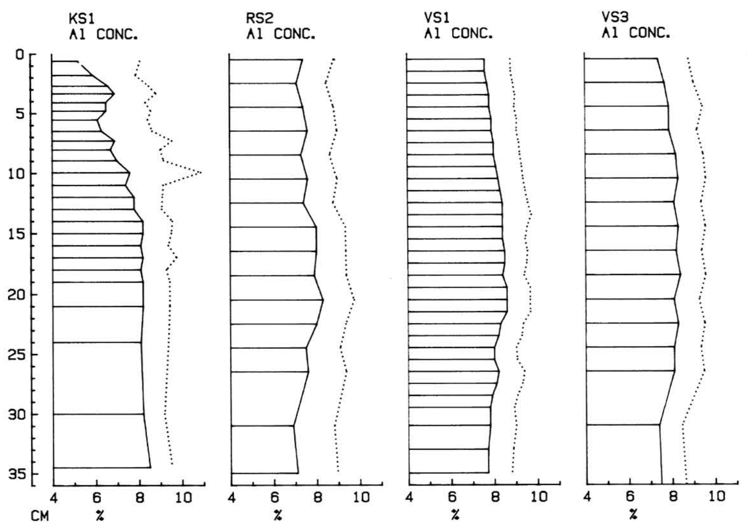


Fig. 15. Aluminum content expressed as a percentage of the dry weight (solid line) and of ash weight (dotted line) of the sediment in the profiles of Lake Vanajavesi.

within the black, laminated sediment) is probably due to the erosion caused by dredging activities. This matter will be discussed later.

5.2.2. *Copper and nickel*

The trace elements copper and nickel belong to the group of elements classified as enriched metals in lake sediments indicating cultural impact (e.g. Kemp et al. 1976, Håkanson 1977a, Förstner & Wittmann 1979). The stratigraphy of copper shows an obvious enrichment in profiles KS1 and VS1 (Fig. 16).

The cultural enrichment factor can be defined as the ratio between the maximum concentration in the surficial layers and the minimum value at the base of the profile ('preindustrial layers', background value). The background value for copper was 69 ppm (KS1) and 35 ppm (VS1). These values are higher than the concentrations reported for Finnish lake and marine sediments, i.e. $<$20 ppm (Hinneri 1974, Heino 1979, Tolonen & Jaakkola 1983). Håkanson (1977a) reports background values of 25-65 ppm for large Swedish lakes. The differences in the decomposition methods make direct comparisons difficult. The total concentrations found in this study are comparable to the values of Håkanson (1977a), who used standard emission spectrographic methods in total metal determinations.

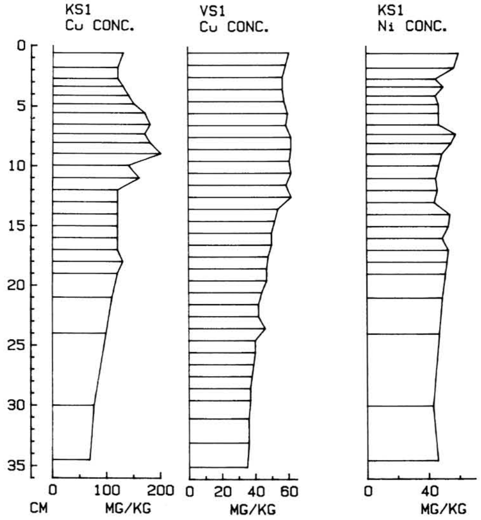


Fig. 16. Copper and nickel content expressed as mg/kg of dry weight of sediment in profiles VS1 (only Cu) and KS1.

The cultural enrichment factor of copper for profile VS1 was 1.8 and for KS1 2.9, using 60 ppm as a background value. If the lower background concentration of VS1 is used for KS1, the cultural enrichment factor is 5.7. The lower layers of core KS1 have been affected by the wastes from Valkeakoski at the beginning of the industrial era (cf. dating of KS1, Fig. 27). The concentrations increase in both cores evenly up to the sediment surface (VS1) and up to 9 cm (KS1). The trend is towards a clear decrease in the uppermost layers of KS1. This is probably due to the low pH of the water during the last two decades. It is not possible to correlate changes in the copper content with any specific source of pollution in the study area. Copper comes from several sources (industrial and municipal waste waters, atmospheric inputs) and the inputs have been evenly increasing in the study area over a long period of time.

The background concentration of nickel in profile KS1 was 43 ppm (Fig. 16). In the Swedish great lakes background concentrations varied between 35-85 ppm (Håkanson 1977a). The cultural enrichment factor was only 1.4. The vertical variations in the profile are small. Nickel is not, therefore, an important pollutant in the study area. The low enrichment of nickel is in good agreement with earlier observations (e.g. Hinneri 1974, Tolonen & Jaakkola 1983).

5.2.3. Lead

Lead was analyzed only from some samples in profile VS1. All the concentrations were lower than 50 ppm. This is within the range of background values in the Swedish great lakes, i.e. 40-135 ppm (Håkanson 1977a). It seems obvious that lead has no important local sources and hence its information value to this study is also limited.

5.2.4. Zinc and cadmium

Zinc and cadmium are related elements which often have a similar distribution in aquatic sediments. Cadmium is also correlated with zinc in the profiles examined (Table 5). The sources and distribution of zinc in the surficial sediments (0-1 cm) were discussed earlier.

The stratigraphy by zinc shows that the background concentration is constant below a level of 30 cm in all four profiles (Figs. 17 and 18). Based on 9 analyses, the mean background for zinc was 260 ± 5 ppm. Håkanson (1977a) reports slightly lower values (100-200 ppm) for large Swedish lakes. The zinc content of Finnish igneous rocks is rather high, being 180 ppm (Lounamaa 1956).

The zinc content and zinc deposition (calculated from sedimentation rates presented in Fig. 26) both indicate a high inrease in zinc loading within the uppermost 30 cm at site KS1 (Fig. 17). The increase of both zinc content and influx is very sharp at a level of 11 cm. In the uppermost 10 cm the concentrations and influx values vary considerably (3900 - 22 000 ppm and 3.6-20.6 g/m^2/year). These figures are exceptionally high. Håkanson (1977a) reports surficial concentrations of up to 10 600 ppm from Lake Vättern (zinc mine pollution). In areas of Lake Mälaren polluted by various metal industries the zinc concentration was below 1000 ppm. The highest concentration reported by Pasternak (1974) from a river polluted by zinc and lead mining and smelting industries in Poland was 20 000 ppm.

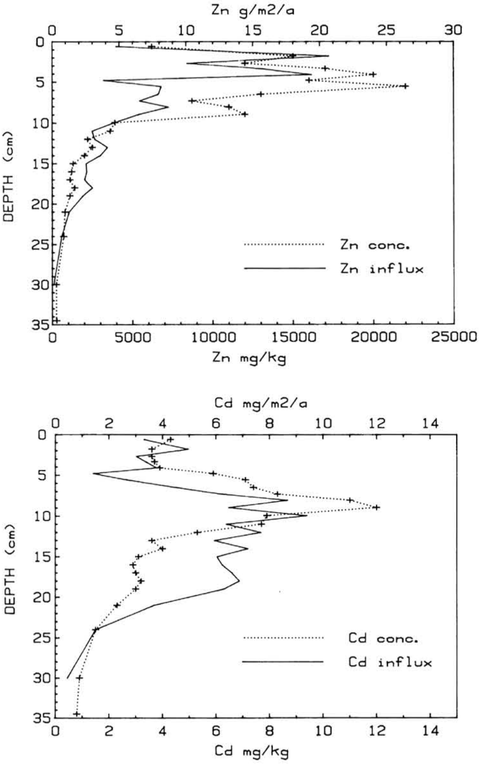


Fig. 17. Zinc content (mg/kg) and influx (g/m^2/year) in profile KS1 (upper figure). Cadmium content and influx in profile KS1 (lower figure).

The rise in zinc content is obvious in the other profiles, too (Fig. 18). The stratigraphy is very similar in cores VS1 and VS3. An increase from the background level begins in both cores from 15 cm. The rise in profile RS2 starts at a markedly lower level (30 cm) than in other cores. The surficial concentrations,

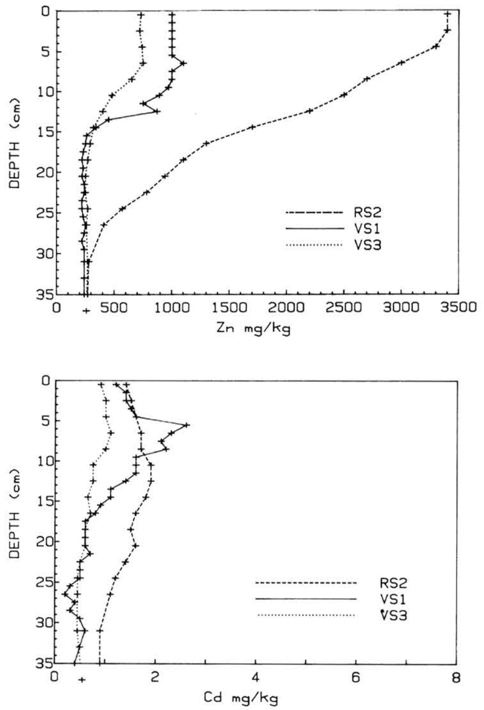


Fig. 18. Zinc content (mg/kg) (upper figure) and cadmium content (mg/kg) (lower figure) in profiles RS2, VS1 and VS3.

cultural enrichment factors and zinc influxes (max. value) for the profiles were as follows:

	KS1	RS2	VS1	VS3
surficial maximum conc. (mg/kg)	22 000	3400	1100	760
cultural enrichment factor	84.6	13.1	4.2	2.9
influx (g/m^2/year)	20.6	4.5	0.54	0.52

Cadmium is clearly enriched in the profiles examined, especially in profile KS1 (Figs. 17, 18). The concentration is quite constant below a level of 30 cm. The background based on 9 analyses is 0.7 ± 0.07 ppm (in the Swedish great lakes 0.5-1 ppm, Håkanson 1977a). Finnish igneous rocks contain 0.3-0.4 ppm (Lounamaa 1956).

The cadmium stratigraphy differs sharply from the zinc stratigraphy in all profiles. Cadmium content and influx increases in KS1 up to 12 ppm (9.2 mg/m^2/year) at a level of 9-10 cm, from which depth the Cd content decreases towards the sediment surface. This decrease is most probably due to the decrease in Cd loading because this kind of decline in the surficial layers can be seen in other profiles, too. The drop in the pH may, however, also be the reason for this trend in Kärjenniemenselkä, but not elsewhere. The critical pH for zinc and cadmium, at which resorption may take place, is about 5.5 (Tolonen & Jaakkola 1983). Profile VS1 shows a higher enrichment of Cd than the other cores. Its maximum content was found at a depth of 5-6 cm (2.6 ppm). The variations in the surficial concentrations were small (Fig. 18). The surficial concentrations (0 1 cm), cultural enrichment factors (surficial / background content) and estimated influxes at the sediment surface for Cd are the following:

	KS1	RS2	VS1	VS3
surficial conc. (mg/kg)	4.3	1.4	1.2	0.9
cultural enrichment factor	6.1	2.0	1.6	1.3
influx (mg/m^2/year)	3.3	1.9	0.6	0.6

In conclusion, zinc shows very clear enrichment in all cores. This enrichment can safely be connected to the highly increased zinc loading in Valkeakoski (cf. Fig. 9). The distribution of cadmium does not, however, follow that of zinc in the uppermost sediment layers. This indicates that the cadmium loading has clearly decreased during the latest stage of the lake development. Cd may have several diffuse sources. The surficial concentrations are at present of the same order of magnitude as reported by Håkanson (1977a) from Åsfjorden, Lake Vänern, where they varied between 1-4 ppm (industrial effluents). In basins loaded by municipal waste waters, concentrations of 1-2 ppm were common (Håkanson 1977a).

5.3. Resin acids

An attempt was made to identify some organic waste substances which could be used as indicators of the effluents of the wood-processing industry in the study area. Recently Salkinoja-Salonen et al. (1981) analyzed the content of some organochlorine compounds in the sediments of Lake Saimaa, Finland. These compounds were released into the water body in bleaching effluents from kraft pulping.

Preliminary analyses of some samples of profile KS1 showed that there were no detectable chlorophenols at this polluted site. Pulp bleaching has not taken place in Valkeakoski.

Table 6. Concentrations of dehydroabietic acid (μg/g d.m.) in profiles KS1, VS1, VS3 and in some surficial sediment samples (0-2 cm). N.D. = not detected.

Depth	Kärjenniemenselkä		Vanajanselkä
(cm)	KS1	VS1	VS3
0-2	1109	8	<2
2-4	491		
4-6	264	3	<2
6-8	23		
8-10	30		
10-12	32	4	<2
12-14	132		
14-16	40		
16-18	83	N.D.	N.D.
18-20	63		
20-22	10		
22-24	2	N.D.	N.D.
26-28	4		
28-30		N.D.	N.D.
30-32	3		
38-40		N.D.	N.D.

Surficial samples:

Rauttunselkä RS2	66	Jumunen	38
Makkaranselkä	78	Liponselkä	37
Konhonselkä	31	Korteselkä	8

Resin acids are important components of wood which are extracted and dissolved in the waste waters during processing at pulp mills. The effluents of both sulphate and sulphite pulp mills contain amounts of these terpene acids high enough for their concentrations in the recipient to be sufficient to exert chronic ecotoxic effects on the aquatic community (e.g. Mäenpää et al. 1968, Fox 1977, Brownlee et al. 1977; effects on fish: Oikari et al. 1980, 1982, Holmbom & Lehtinen 1980).

Dehydroabietic acid is usually the main component of the resin acids in the effluents of the pulp industry (Mäenpää et al. 1968). While it is a minor constituent (2 %) of the resin acids in pine wood, its proportion increases strongly during the pulping process and especially in the distillation of tall oil (Kahila 1971). Most of the resin acids are apparently readily degraded in the receiving watercourse, but because of the stability conferred by its aromatic ring structure dehydroabietic acid (later DHAA) is likely to be more persistent than other resin acids (e.g Fox 1977).

Resin acids were analyzed from some samples of three profiles (KS1, VS1 and VS3) and six surficial samples (0-2 cm) in order to examine their vertical and horizontal distribution in relation to the possible source of pollution (wood-processing industry in Valkeakoski). The main emphasis was placed on DHAA, which was the most abundant resin acid in sediments from Vanajavesi (other identified resin acids were sandaracopimaric, abietic, pimaric and isopimaric acids). Kärjenniemenselkä receives the waste waters of kraft and sulphite pulp mills. There is also a tall-oil distillery which may contribute a high load of resin acids to Kärjenniemenselkä. The surficial concentration of KS1 is very high compared to other sampling sites, being over 1 mg/g (Table 6). In other samples the concentration varied between 1-78 μg/g.

The decrease in DHAA-concentration of the sediment as a function of distance from the pollution source may be due to dilution, sedimentation and degradation in the water phase. When the decrease is compared with that of zinc (Fig. 19), it can be seen that DHAA-concentration decreases more rapidly than zinc as a function of distance. The decrease is especially sharp within the first few kilometres. The decrease of zinc is mainly a function of simple dilution and sedimentation. The results indicate that microbial degradation is probably important in the case of DHAA. The degradation processes are probably more effective in the heavily polluted water areas than elsewhere in the study area (cf. Brownlee et al. 1977). Rather high concentrations are, however, analyzed from water areas at a distance of up to 22 km downstream from Valkeakoski. It seems probable that there are additional inputs of DHAA at a distance of 18 km, where there is a small plywood-factory in the village of Viiala. This kind of increase in the DHAA-concentration may also result from log floating activities (cf. Fox 1977).

Upstream from KS1 the DHAA-concentrations are lower than in the lower course of Vanajavesi. The difference between DHAA and zinc is also remarkable. The concentrations of DHAA are low at VS1 and VS3. It must be remembered that the waste water from the Valkeakoski area were only dispersed into Vanajanselkä in wintertime. There is no constant loading of this area by resin acids and there is more time for the latter to be degraded until they increase the concentration in the

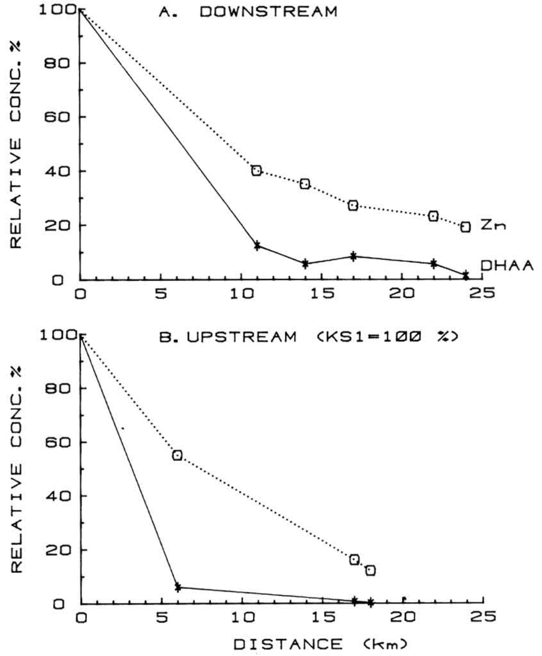


Fig. 19. Relative concentration expressed as a percentage of the concentration of profile KS1 (0-2 cm) of dehydroabietic acid and zinc in the surficial sediments at sampling stations downstream from Valkeakoski (A. stations: KS1, Makkaranselkä, Konhonselkä, Jumunen, Liponselkä, Korteselkä, cf. Fig. 1) and upstream from Valkeakoski (B. stations: KS1, RS2, VS1 and VS3.

sediments. In contrast, all or most of the zinc input is sedimented.

It is known that sediment often effectively prevents the microbial degradation processes. Brownlee et al. (1977) reported, however, that DHAA slowly degrades microbially in the sediment layers. They suggested that the minimum half-life of the disappearance of DHAA in the sediments was 21 years. They could not take into account possible changes in the DHAA-loading when interpreting their profiles. Fig. 20 shows the DHAA-content and influx values in profile KS1. The decrease is exponential in the uppermost 7 cm of the core, which reveals that microbial degradation is important even in the uppermost sediment layers. Changes in the resin acid loading cannot explain this decrease. Below this layer, however, the degradation processes seem to be less important, and DHAA content is probably dependent mostly on the DHAA input to the lake. Profile KS1 shows that there are slightly elevated concentrations at a level of 30-32 cm

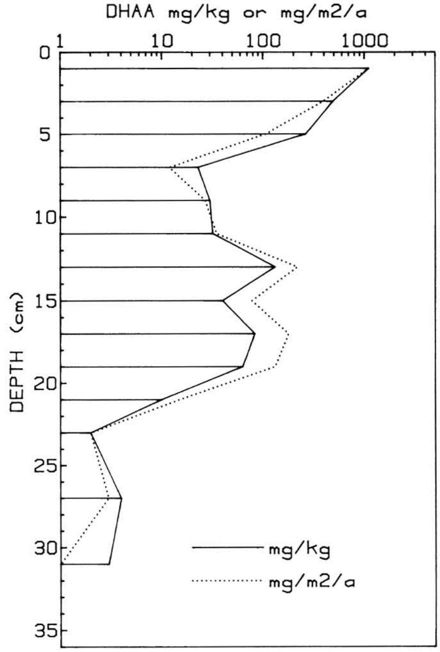


Fig. 20. Dehydroabietic acid content (mg/kg) and influx (mg/m^2/year) in profile KS1.

in KS1, which indicates a low impact from the wood-processing industry. There is a sharp increase in the DHAA loading in a level of 23 cm.

Other profiles from Vanajanselkä (Table 6) show only a slight enrichment of DHAA in the uppermost 12 cm (VS1). In profile VS3 the surficial concentrations are very low. The difference between these cores is logical because VS1 has been under direct pressure from the waste waters of the wood-processing industry during the wintertime.

Brownlee et al. (1977) analyzed DHAA-concentrations from surficial sediments of a part of Lake Superior, Canada. The area was polluted by a kraft pulp and paper mill. The surficial concentrations varied between 1.5-101 μg/g. The areal distribution clearly indicated the distribution of the waste waters of the pollution source. Elevated concentrations were measured at a distance of about 15 km from the mill.

The results show that DHAA-concentration of the surficial sediments can be indicative of the waste waters of the wood-processing industry. It must be taken into account that additional inputs can be due to local sources (e.g. log floating). Microbial degradation clearly affects the absolute concentrations in the water column and uppermost sediment layers. It seems probable that the concentration becomes more stabile and dependent on the changes in the absolute load in the deeper sediment layers (below 5-10 cm). It also appears that microbial degradation is most effective in the immediate vicinity of the pollution outfall.

5.4. Age-depth distributions

5.4.1. Laminated sediment of profile KS1

The adhesive tape peel preparations made from the freeze-dried surface of the uppermost 11.5 cm of profile KS1 supported the view that the laminations are annual varves like those reported from many smaller lakes or ponds (e.g. Simola 1979, 1983 and references therein). The diatom flora showed rhythmic changes reflecting annual cycles (Simola 1983). The species composition was poor (*Melosira ambiqua, M. distans, M. granulata* var. *angustissima, M. italica* and *Tabellaria flocculosa* were the most abundant species).

The sediment was entirely black except for thin greyish layers clearly visible in the wet sediment (Fig. 21). The diatom abundance minimum regularly occurred just below these layers. It seems probable that this minimum represents the winter and that the greyish layers are deposited during the spring floods. The physico-chemical data shows that water at 10 m is totally anoxic almost throughout the year. This means that black FeS-gyttja is deposited continuously.

Two greyish layers at a depth of 9.2-10.1 cm were deposited, according to the varve chronology, in the years 1960-61. The archives of the local water building authority (Hyppönen, pers.comm.) showed that about 25 000 m^3 of clayey bottom material was dredged in the vicinity of KS1 in order to change the route for boat traffic. The working periods were May 5th 1960 - January 5th 1961 and June 1st 1961 - September 18th 1961. This agrees well with the varve chronology. The erosion layer is thicker in another core taken near this dredging area.

Varve counting shows that regular laminations started to form in 1957. This means that at this depth the hypolimnion then became regularly anoxic and the bottom dwelling zoobenthos vanished, or at least drastically decreased. This is the case according to the chironomid stratigraphy analyzed by Kansanen (1985). According to Kansanen & Aho (1981), site KS1 was totally desolate in the years 1965 and 1971 and the fauna was very sparse in 1977. The diffuse black striae in the layers below 11.5 cm (Fig. 21) reflect seasonal periods of oxygen depletion.

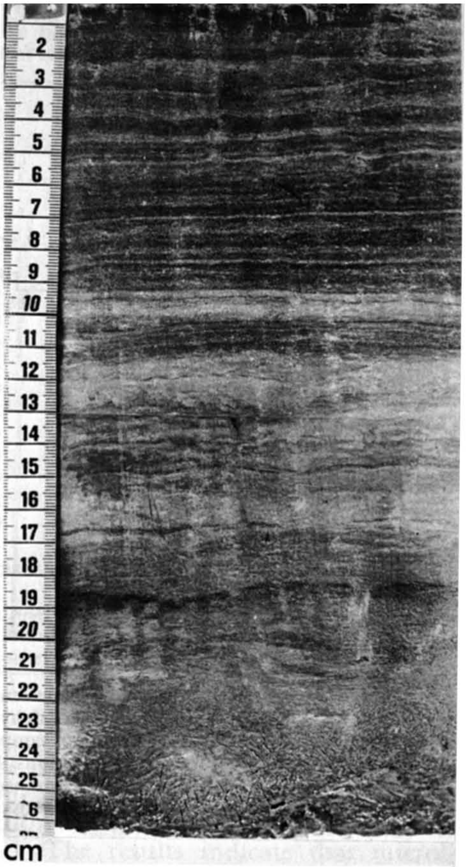


Fig. 21. A frozen core from the uppermost 26 cm of partly laminated sediment of the site KS1.

Varve counting showed that the sedimentation rate has varied during the last 23 years between 2.0-12.0 mm. The thickest varves were in the surficial layers, which are not yet compacted. The dry mass sedimentation rate has varied between 24-138 $mg/cm^2/year$ (in average 70 $mg/cm^2/year$ for the years 1957-1981). Such variations are not surprising in a flow-through basin like Kärjenniemenselkä, where the sedimentation rate is affected by variations in the mean flow and in the waste water loading.

Below a level of 11.5 cm the identification of varves on the basis of diatom analysis was not possible. However, black striae are clearly visible in the dark grey sediment (Fig. 21). If it is assumed that these striae represent the annual summer stagnation, this means that there was a markedly higher sedimentation rate below 11.5 cm than in the uppermost layers.

5.4.2. *Artificial radionuclide chronology*

Atmospheric nuclear weapons tests have produced a global fallout amounting to several radionuclides. The behaviour of these radionuclides has been extensively studied over the past 25 years. Among the most extensively investigated nuclides have been ^{90}Sr and ^{137}Cs, and since the beginning of the 1970s ^{239,240}Pu. The deposition rates of these radioactive nuclides have been determined regularly at several locations around the world. The annual deposition rate has been strongly correlated with the frequency of nuclear testing.

The distribution and migration of fallout radionuclides in soil and sediments have constituted an object of interest since the middle of 1950s. The possibility of using the distribution of ^{137}Cs in sediment profiles for the dating of sediment layers was not recognized until the beginning of the 1970s (e.g. Pennington et al. 1973). Since then several investigators have used ^{137}Cs and also ^{239,240}Pu for the dating of recent sediments. The annually laminated lake sediments have been used to prove the reliability of the ^{137}Cs- and ^{239,240}Pu-derived estimates of sediment age. The ages obtained using the distribution of ^{137}Cs and ^{239,240}Pu were compared with ages calculated directly by counting annual laminations (Jaakkola et al. 1983). A similar distribution of ^{137}Cs and ^{239,240}Pu was found in the lakes studied.

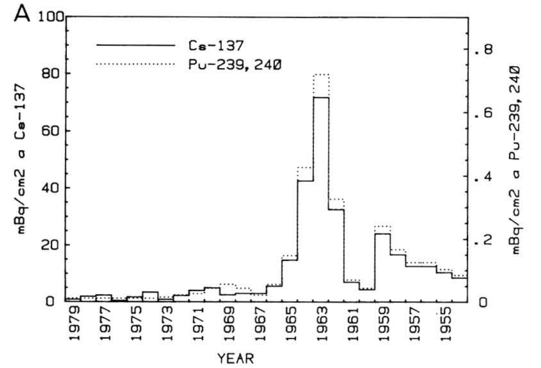
Fig. 22A shows the deposition rates of ^{137}Cs and ^{239,240}Pu in the Helsinki area, Finland, during 1955-1979. The calculations are based on the deposition determinations of ^{137}Cs in southern Finland during 1970-1981 (Institute of Radiation Protection 1982) and on the ^{137}Cs and ^{239,240}Pu analyses of surface air samples collected in Helsinki during the period 1962-1977 (Jaakkola et al. 1979). The deposition values for the 1955-1961 period were estimated using the values for the deposition rate in New York (Wrenn 1974) and the ratio of ^{137}Cs and ^{239,240}Pu concentrations in the surface air of Helsinki compared to those of New York in 1962-1979. A clear maximum of radioactive fallout produced by atmospheric nuclear tests occurred during 1962-1964 and a lower peak occurred in 1958-1959. The deposition rate of ^{137}Cs and ^{239,240}Pu was negligible prior to 1954.

The upper part of sediment profile KS1 was annually laminated. A clear-cut maximum of the ^{137}Cs concentration was found at a depth of 9-10 cm (Fig. 22B). This corresponds with the period of maximum fallout, 1962-1964. The decrease of the ^{137}Cs concentration found at a depth of 12-13 cm may indicate sedimentation in 1954-1955.

In the case of profile RS2, no clear maximum up to a depth of 20 cm was found (Fig. 22C). The ^{137}Cs profile indicates strong disturbances at this sampling site.

The distributions of ^{137}Cs and ^{239,240}Pu at sampling sites VS1 and VS3 show a broad maximum at a depth of 9-12 cm which probably corresponds to the sedimentation during the first half of the 1960s (Fig. 22D and E). The maximum is clearer for ^{239,240}Pu than it is for ^{137}Cs. The rapid decrease of ^{137}Cs and ^{239,240}Pu concentrations at VS1 suggests that the sediment at a depth of about 15 cm originates from the mid-1950s. Compared to a profile KS1, it is evident that the sediments at VS1 and VS3 were affected by heavy mixing. ^{137}Cs and ^{239,240}Pu have quite a similar distribution in the sediments of VS1 and VS3.

In 1979 (for KS1 in 1981) the calculated total amount of ^{137}Cs accumulated per unit area in sediment cores was 405, 700, 370 and 400 mBq/cm^2 (100, 180, 100 and 110 mCi/km^2), respectively. The values of KS1, VS1 and VS3 are similar and reveal regular sedimentation at these locations. The total accumulated amount of ^{137}Cs at RS2 shows highly increased sediment focusing. The total contents of ^{137}Cs in sediment cores analyzed are in agreement with the cumulative deposition value of ^{137}Cs in Milford Haven, U.K. (51.5°N, 5°W). Cambray et al. (1982) have reported a value of 90 mCi/km^2 for the year 1979. The total accumulated amount of ^{239,240}Pu was 5.9 and 3.1 mBq/cm^2 (1.6 and 0.84 mCi/km^2) for sediment cores VS1 and VS3, respectively. Hardy et al. (1973) have reported 1.6 ± 1.0 mCi/km^2 for cumulative



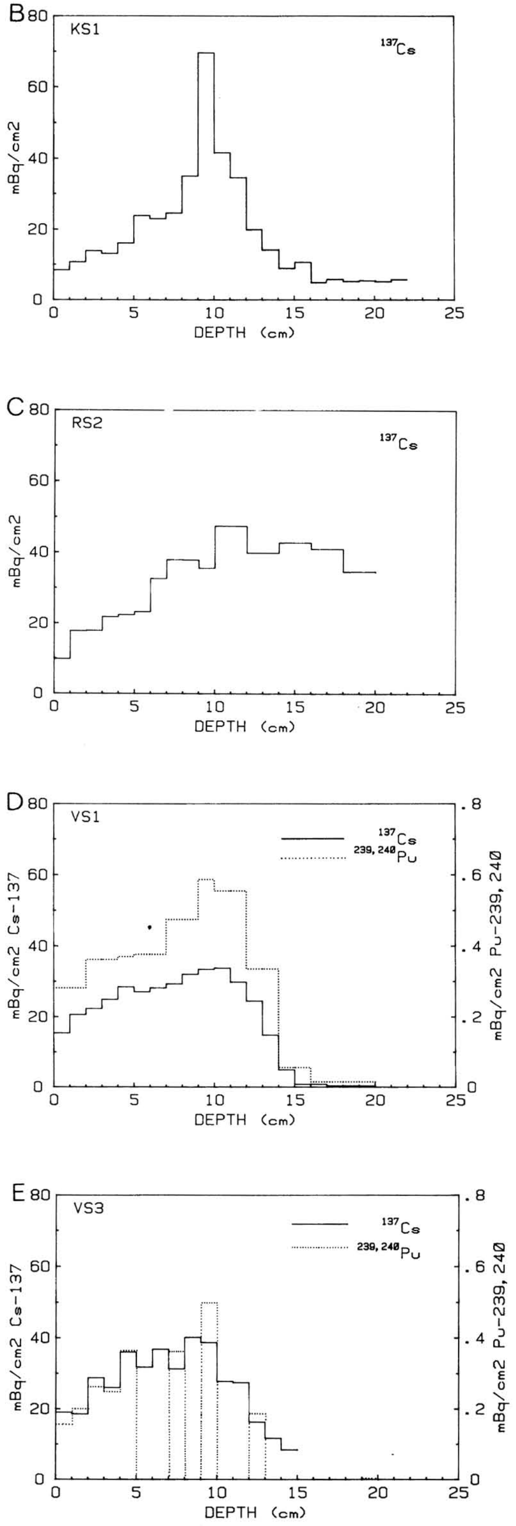


Fig. 22. A. The deposition rate of ^{137}Cs and ^{239,240}Pu in southern Finland during 1954-1979. B-E. Distribution of ^{137}Cs and ^{239,240}Pu in profiles of Lake Vanajavesi (in VS3 Pu-analyses were made only from slices of 0-5, 7-8, 9-10 and 12-13 cm).

^{239,240}Pu fallout at a latitude of 60-70°N. According to Simola et al. (1979), the total content of ^{239,240}Pu fallout in Baltic Sea sediments ranged from 2.2 to 12.3 mBq/cm^2 (0.6-3.3 mCi/km^2).

5.4.3. Lead-210 chronology

^{226}Ra is a member of the uranium-238 decay series. ^{226}Ra is present in the crustal material and decays to ^{222}Rn, which is a radioactive noble gas. Radon escapes from the ground into the atmosphere and decays through a series of short-lived nuclides to ^{210}Pb (half-life 22.3 years). The residence time of ^{210}Pb in the atmosphere is about one week and it is deposited through wet precipitation and dry fallout directly from the air. ^{210}Pb can also be introduced into surface waters through the weathering of soil and effluents discharge from groundwater. In a water column ^{210}Pb is rapidly transferred into sediments. This excess of ^{210}Pb (unsupported ^{210}Pb) decays towards a certain background level in sediment. This background level (supported ^{210}Pb) is produced in situ through the decay of ^{226}Ra.

It can be assumed that in the sediment layers considered in this study there exists a radiochemical equilibrium between ^{226}Ra and supported ^{210}Pb. In the profiles investigated the sediments are homogenous fine clays having the same geological source. Therefore, it is assumed that the ^{226}Ra concentration is constant in the samples analyzed and the quite stable ^{210}Pb content found in deeper layers is used as the content of supported ^{210}Pb, which is subtracted from the total content to give the content of unsupported $^{210}\mathrm{Pb}(^{210}\mathrm{Pb}_{uns} = {}^{210}\mathrm{Pb}_{tot} - {}^{210}\mathrm{Pb}_{sup})$.

5.4.3.1. The C.I.C. and C.R.S. models of ^{210}Pb distribution

In undisturbed sediment cores, where the sedimentation rate is constant, the content of unsupported ^{210}Pb decreases exponentially with increasing depth of sediment. This exponential decrease was first applied to sediment dating by Goldberg (1963), but has come into general application only within the past few years (lake sediments Krishnaswami et al. 1971).

There are several alternative 'models' for the distribution of ^{210}Pb in sediments (cf. reviews of Robbins 1978, Krishnaswami & Lal 1978). The usual assumptions are: (1) the flux Φ (mBq/cm^2/year) of unsupported ^{210}Pb is constant to the sediment-water interface, and (2) there is no migration of ^{210}Pb in the sediment over the dating interval, i.e. the change in the concentration of the nuclide is due solely to its radioactive decay.

If both the flux of ^{210}Pb (Φ) and the sedimentation rate S (g/cm^2/year) are constant, then the initial activity at the sediment-water interface ($A_o = \Phi / S$) has been constant, too. In this case the activity of the nuclide in the sediment at any depth (z) from the sediment-water interface is given by:

$$A(z) = A_o e^{-\lambda t},$$

where λ = the radioactive decay constant of ^{210}Pb and t = the age of the sediment at depth z. This is the 'constant initial concentration model (C.I.C.)'.

If the sedimentation rate has changed during the dating interval, but the flux of unsupported ^{210}Pb has remained constant, the ages of different strata in the sediment profile can be calculated from the integrated activity of ^{210}Pb (Goldberg 1963, Appleby & Oldfield 1978). The time t required to deposit a sediment layer of thickness z in a sediment core with a constant radionuclide flux is:

$$t = (1/\lambda)\ln|Q_o/Q(z)|,$$

where Q_o = the cumulated activity of the nuclide below the sediment-water interface and $Q(z)$ = the cumulated activity remaining below depth z from the surface.

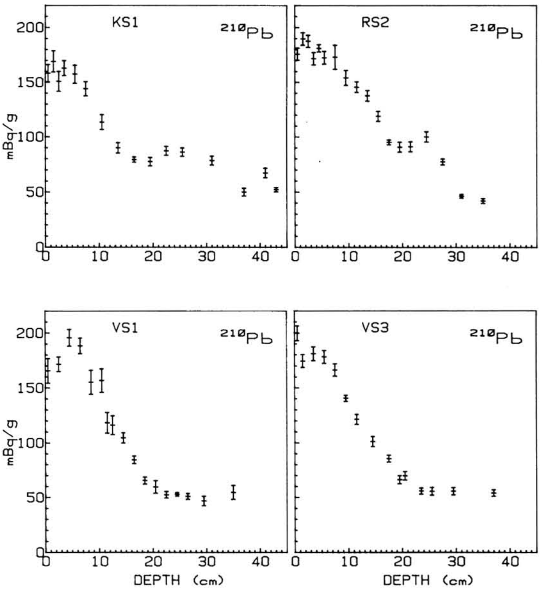


Fig. 23. Total ^{210}Pb content versus depth in profiles of Lake Vanajavesi. The standard deviation of radioassay (1 σ) is indicated.

For a detailed description of the calculation of this 'constant rate of supply model (C.R.S.)', see Appleby & Oldfield (1978). Since a new value of $Q(z)$ is available for various depths in the profile, it it possible to calculate the age of the sediment slices and hence the sedimentation rates. In the annually laminated Finnish lake sediments this C.R.S. method gave excellent results (Appleby et al. 1979).

The vertical distribution of the total ^{210}Pb concentration in the profiles is presented in Fig. 23 (cf. Appendix 1). Profiles VS1 and VS3 are in principle similar. In both profiles the concentration reveals a continuous almost exponential decrease up to a depth of about 20 cm towards the fairly constant natural background level indicated by the long tail of the curve. In both profiles, however, the surficial (5 cm) concentrations are considerably lower than expected. In profiles KS1 and RS2 the decrease towards background level is more irregular. In both profiles there is another peak in addition to the surface maximum just below the 20 cm level.

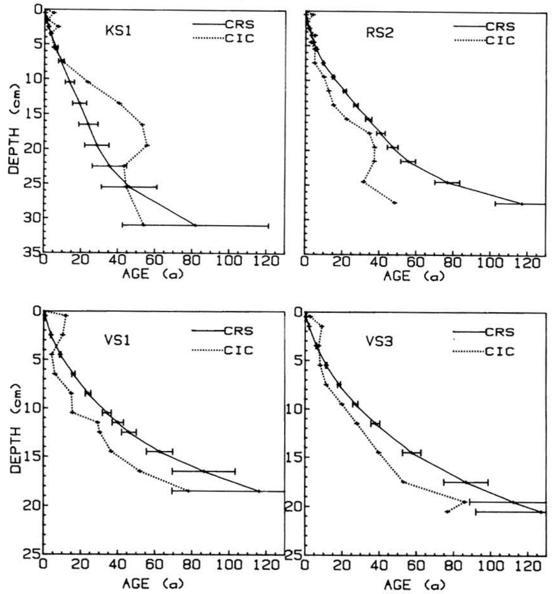


Fig. 24. Age-depth curves based on C.R.S. and C.I.C. models of ^{210}Pb dating for profiles of Lake Vanajavesi. The standard deviation of radioassay (1 σ) is indicated for C.R.S. curves.

The vertical distribution of the ^{210}Pb concentration indicates that none of these profiles is ideally suitable for the use of the simple C.I.C. model because the decrease in the concentration curve does not follow the exponential change over the whole dating period. The age-depth distributions (Fig. 24) obtained using the C.I.C. and C.R.S. models show that the C.I.C. model is more suitable for profiles VS1 and VS3 than for profiles KS1 and RS2. The ages derived from the C.R.S. model are markedly longer than the C.I.C. ages, especially for the lower layers of the profiles. If only the smooth age-depth distribution curves obtained by the C.R.S. model are considered, it could be concluded that the C.R.S. model can be used even for the 'kinked' profiles of KS1 and RS2.

5.4.3.2. The steady-state mixing model

Both the C.I.C. and C.R.S. models require that ^{210}Pb does not migrate in the sediment column. In the annually laminated lake sediments, where particle reworking processes are absent, a good agreement in dating was obtained between the C.R.S. model and varve counting (e.g. Appleby et al. 1979, Tolonen & Jaakkola 1983).

In the homogenous lake sediments both biological and physical activities occurring near the sediment-water interface may, however, result in lateral and vertical redistribution and displacement of sediments. These processes can markedly alter the concentration profiles of stratigraphic markers (e.g. pollen grains) and other chemical and radioactive tracers up to several centimetres below the sediment-water interface (e.g. Davis 1974, Guinasso & Schink 1975, Håkanson & Källström 1978).

Recently, e.g. Edgington & Robbins (1975, 1976), Robbins & Edgington (1975), Robbins et al. (1977, 1978, 1979) and Robbins (1982) have paid attention to the significance of bioturbation and other mixing in the redistribution of radioactive tracers in lake sediments. Table 7 shows that bioturbation caused by the bottom fauna can also be an important factor in Lake Vanajavesi. Only site KS1 has been barren during recent times, thus enabling a laminated structure to be preserved. Elsewhere there is an abundant macrozoobenthos burrowing in the uppermost sediment layers (mainly chironomid larvae, such as large-sized *Chironomus*, oligochaete worms, and earlier also a crustacean, *Pontoporeia affinis*, see Kansanen & Aho 1981). The population densities of the meiozoobenthos (mesh size range 0.6-0.1 mm) can be as high as 70 000 ind./m^2 in the profundal of Vanajanselkä (Kansanen 1981). The macrozoobenthos is clearly more abundant at sites VS1 and VS3 than it is at RS2 in Rauttunselkä, where the oxygen conditions are at present unfavourable to bottom animals (Table 7). *Chaoborus flavicans* favours an oxygen-poor environment and is clearly more abundant at RS2 than elsewhere. On the other hand, large *Chironomus*-larvae are almost absent at RS2.

There are no direct observations on the vertical occurrence of zoobenthos in the sediment layers of Vanajavesi. According to Särkkä & Paasivirta (1972), on average 58 % of the total macrozoobenthos occurred in the uppermost 2 cm and 87 % in the uppermost 6 cm in the sediments of Lake Päijänne, Finland. For the meiozoobenthos the corresponding figures were 78 % and 99 %. In the polluted areas comparable to Vanajavesi the macrofauna lived deeper down in the sediment than it did in the cleaner parts of the lake (27 % below 6 cm).

Table 7. The abundance of the macrozoobenthos (exx./m^2) in August 1971 at the coring sites. Figures are based on 20 samples taken with a Kajak-corer and sieved through a 0.6 mm sieve (Kansanen, unpublished).

	KS1	RS2	VS1	VS3
Limnodrilus hoffmeisteri	–	132	–	33
Potamothrix hammoniensis	–	198	165	560
Procladius sp.	–	33	132	33
Chironomus anthracinus	–	–	1744	1316
Chironomus neocorax	–	–	987	526
Chironomus plumosus	–	66	–	–
Chaoborus flavicans	–	1250	33	691
Total fauna	–	1679	3061	3159

There is additional evidence on bioturbation in the ^{210}Pb, as well as in the ^{137}Cs and ^{239,240}Pu, profiles. According to Robbins (1982), a surficial zone of nearly constant ^{210}Pb and ^{137}Cs is typical to bioturbated profiles, and this kind of zone can also be seen in the profiles of metal contaminants. It can be seen that there is a zone of constant zinc concentration (down to 6–7 cm) in profiles VS1 and VS3 (Fig. 18) despite the highly increased zinc inputs to the lake (Fig. 9). The thickness of this zone agrees well with the ^{210}Pb concentration in both profiles (a break in the exponential rise at the same depth). The shape of the distribution curve of ^{137}Cs and ^{239,240}Pu in both profiles is similar to those reported by Edgington & Robbins (1975) from Lake Michigan.

It is clear that disturbances during coring and slicing also cause redistribution in the loose surficial layers of the profiles. It is, however, very unlikely that this would have significantly affected the observed stratigraphy of the profiles. The sampling procedure used for all profiles preserved the ^{137}Cs and zinc stratigraphy undisturbed in the annually laminated core KS1. The possibility of physical mixing is also slight, as all the sites were selected from area where the resuspension activity is most likely minimal.

Robbins & Edgington (1975) presented a quantitative steady-state mixing model accounting satisfactorily for the observed heavy metal and radionuclide profiles which were affected by surficial mixing. In this model (see also Robbins 1982) the mixing is assumed to occur only in the sediment column as a result of rapid steady-state (biological or physical) activity, over a zone of fixed thickness (s) at the sediment-water interface. As the thickness of the sediment column increases over time, this zone moves upward at the sedimentation rate ω (cm/year). In the case of ^{210}Pb the flux to the sediment-water interface is assumed to be constant.

According to this model, the activity in the mixed zone (A_m) is:

$$A(z) = A_m = \gamma A_s / (\gamma + \lambda),$$

when $z \leq s$ and where $A_s =$ the activity of the newly incoming materials, $\gamma = \omega / s$ and $\lambda =$ radioactive decay constant of ^{210}Pb.

Below the mixed zone ($z > s$) the activity is given by the equation:

$$A(z) = A_m{}^{-\lambda(z-s)/\omega}$$

The sedimentation rate derived from this equation is assumed to be constant in the profile.

The premises for the use of this steady-state mixing model are sufficient in profiles VS1 and VS3. In both of them there is a surficial zone of constant zinc concentration (Fig. 18). In this zone the ^{210}Pb-activity is suppressed and below it there is an exponential decrease down to the level of supported ^{210}Pb (Fig. 23). There are no indications of remarkable changes in the sedimentation rate at these sites. The ^{137}Cs and ^{239,240}Pu profiles are typical of bioturbated profiles. The mixing model is not applicable to sites KS1 and RS2.

The steady-state mixing model was fitted to the observed ^{210}Pb-profiles of VS1 and VS3 by the least-squares method (Fig. 25). This model seems to fit both profiles well. The sedimentation rates were 0.4 cm and 0.6 cm, the dry mass sedimentation rates were 54 mg/cm^2/year and 71 mg/cm^2/year and the inferred mixing depths were 7.3 cm and 6.1 cm for profiles VS1 and VS3, respectively. Such mixing naturally increases the odds against obtaining historical records from sediment layers. Two discrete depositional events (time difference T years) become essentially unresolvable, if T is shorter than the residence time of the sediment material within the mixed zone. This time, called time resolution (T_r), is given by the ratio of the mixed depth to the sedimentation rate (Robbins 1982):

$$T_r = s/\omega = \gamma^{-1}$$

The time resolution of profile VS3 (16.1 years) was shorter than that of VS1 (24.4 years).

5.4.3.3. *The flux of unsupported ^{210}Pb to sediments*

The flux rates of unsupported ^{210}Pb estimated from the C.R.S. model were for profiles KS1, RS2, VS1 and VS3 10.6 ± 1.1, 18.0 ± 0.4, 11.0 ± 0.3 and 11.6 ± 0.3 mBq/cm^2/year, respectively. Although these figures are subject to the same possible errors as the C.R.S. model itself, they indicate that the flux at site RS2 is markedly higher than elsewhere. Other profiles are very similar in this respect. Robbins (1982) has estimated the flux rates of ^{210}Pb over the Great Lakes as about 20 mBq/cm^2/year. Very variable figures (range 4.4–50.3) were reported by Oldfield et al. (1980). The total cumulative residual unsupported ^{210}Pb contents of profiles KS1, RS2, VS1 and VS3 were 340.4, 577.2, 351.5 and 373.7 mBq/cm^2, respectively.

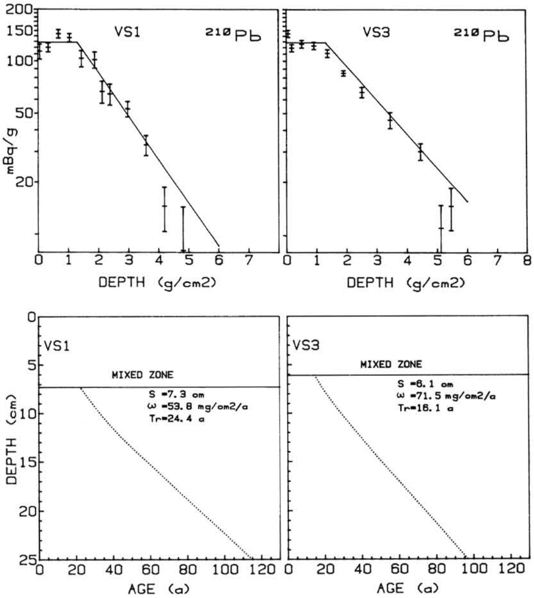


Fig. 25. Unsupported ^{210}Pb content versus depth in profiles VS1 and VS3 (semilogarithmic presentation) and best fit of the steady-state mixing model of Robbins & Edgington (1975) on observed values. The standard deviation of radioassay (1 σ) is indicated. Age-depth curves (below the mixed layer) based on the steady-state mixing model for profiles VS1 and VS3. The best values obtained from mixing model for the depth of mixed zone (S), sedimentation rate (ω, mg/cm^2/year dry mass) and time resolution (T_r) are given.

6. Discussion

6.1. Determination of the bottom dynamic conditions

The analysis of the grain-size distribution of the surficial sediments and the visual characterization of the lithostratigraphy of the cores showed that there is unexpected current activity in the deep-water region of the main basin of the study area, Vanajanselkä. In small basins there appears to exist a uniform 'critical depth', below which the conditions are suitable for undisturbed accumulation. The bottom dynamic map (Fig. 8) shows that the deep-water transportation bottoms are located mainly in the long and narrow depressions of the southwestern sub-basin of Vanajanselkä. It is obvious that these transportation processes explain the bottom morphology of the basin and why these narrow depressions have not been filled by the basin-fill effect during the lake history. According to Hiltunen & Kansanen (1983a, 1983b) a probable explanation for the high dynamic energy level in the deep-water region of Vanajanselkä are the periodical water movements caused by seiche or internal seiche. Similar deep-water erosion or transportation bottoms have been reported from large lakes, e.g. by Sly et al. (1982).

These observations serve to clearly underline the importance of selecting representative coring sites in complex lake basins. Erosion bottoms are easy to identify. Transportation bottoms, where long periods of accumulation of fine sediments are interrupted by short episodes of erosion due, e.g. to storms, are difficult to separate from accumulation bottoms. Håkanson (1977b, 1981a, 1981b, 1981c) and Håkanson & Jansson (1983) have offered several ways of determining the bottom dynamic conditions in a basin from simple morphometric parameters, using the water content of the surficial sediment (0–1 cm) as a key parameter. It is clear, that these methods can only give a rough picture of the real conditions. The results of this work demonstrate that the water content has little information value, at least in very fine-grained deep-water sediments. The water content is correlated with the mean particle size, but for clay size area ($\Phi > 8$) the correlation becomes increasingly poorer with decreasing grain size, since many factors other than the grain size regulate the water content (cf. Håkanson & Jansson 1983). There are also methodological difficulties in accurately determining the water content of the uppermost centimetre, because the sediment-water interface is often diffuse. Similar limitations apply to the use of organic content. The organic content is dependent on local organic inputs (detritus, organic waste waters). Thus, it has only limited value and can be used only within a small area to indicate regions where accumulation occurs (cf. Hargrave & Kamp Nielsen 1977).

The results of this study support the use of the analysis of the grain-size distribution of the surficial sediments in the mapping of the basin of accumulation. With the aid of higher order statistical measures (standard deviation, skewness and kurtosis), it is possible to obtain more information from the distribution curve in numerical form than simply by using the value of mean particle size (or water content). There are several ways of using the grain-size parameters (e.g. Folk & Ward 1957, Folk 1966, Solohub & Klovan 1970, Sly 1978, Reineck & Singh 1980). Sly et al. (1982) prefer the use of the skewness/kurtosis relationship, by which it is possible to classify samples into several categories having different dynamic energy levels. It is clear that this relationship is not always useful. When most samples have a normal or near normal distribution, as in this study, the standard deviation may be the most useful parameter (cf. Sly et al. 1982). In Lake Vanajavesi nearly all samples belonged to the clay category owing to the ready availability of clay-size materials. Standard deviation was able to identify the small, but hydrodynamically significant deviations from the unimodal clay population, the grain-size distribution of which was typical of undisturbed accumulation bottoms.

As was pointed out by Reineck & Singh (1980), there are several limitations in the use of grain-size parameters as indicators of sedimentary environments. The grain-size distribution is a product of the hydrodynamic factors of an environment. Similar grain-size distributions may result in rather different environments. The availability of sediment materials is also an important limiting factor. Hence, it is not possible to create a universally valid classification of the grain-size distributions typical of a particular sedimentary environment in different lakes (cf. also Solohub & Klovan 1970). Although the separation of sedimentary environments (e.g. beach, eolian, channel, lake delta environment) is not possible, it is quite easy to distinguish between high- and low-energy environments within a single basin. Areas dominated by river action should be separated from those dominated by wave action. The results of the present work show that the granulometric analysis of the surficial sediments is a useful method in delineating the areas best suitable for taking representative cores not affected by resuspension activity. The best results can be achieved when echo-sounding and visual characterization of the surficial sediments are also made.

6.2. Evaluation of the dating methods on the basis of the core stratigraphy

A reliable chronology provides a fundamental basis for the interpretation of both chemical and biological sediment records in palaeolimnological investigations. Despite recent progress in this area, an acute problem still exists in most cases, especially when sediments are not laminated. Even when laminated structures do occur, a possibility of intra-annual varves (Simola & Tolonen 1981) or secondary structures (e.g. Håkanson & Källström 1978) needs to be taken into account. The annuality of the varves should, therefore, always be verified by microscopical observations of the seasonal successions of biological remains such as siliceous algae (Simola & Tolonen 1981).

A sediment chronology obtained from the distribution of radioactive isotopes (natural radionuclides or artificial 'bomb' nuclides) has a direct application to recent sediments where signs of pollution are apparent. There has been a dramatic growth in the use of ^{210}Pb and ^{137}Cs in sediment dating during the last few years (cf. reviews of Krishnaswami & Lal 1978, Robbins 1978 and Appleby & Oldfield 1983). These isotopes, and in some cases also ^{239,240}Pu, have been used for a large number of different water bodies having different sedimentation conditions. Too little attention has been paid to the premises for the use of the selected method or dating model in the case in question. Robbins (1978) and Appleby & Oldfield (1983) pointed out that there is no single model that will furnish a reliable ^{210}Pb chronology in all cases and that each data set must be evaluated independently for consistency with one or other of the dating models. The present work clearly demonstrates this. The four profiles selected for the detailed analyses are different in several respects (sedimentation rate, mixing of surficial layers, and sediment focusing at the coring site).

There are some favourable features in the stratigraphy making it possible to evaluate the reliability of the derived age-depth distributions and dating methods. The most valuable of these is the occurrence of annually laminated sediments in one profile. The typical stratigraphy of the major inorganic pollutant, zinc, which can be linked to the known loading history, supports the evaluation, as do the biostratigraphic changes in the profiles (Kansanen 1985).

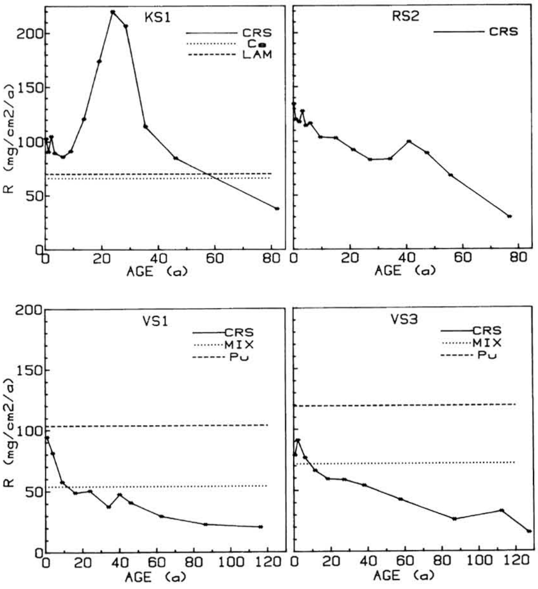


Fig. 26. Comparison of different methods for the estimation of dry mass sedimentation rate for the profiles of Lake Vanajavesi. LAM: based on annual varve chronology. Cs or Pu: based on distribution of ^{137}Cs or ^{239,240}Pu in sediment. CRS: based on C.R.S. ^{210}Pb dating model (Appleby & Oldfield 1978). MIX: based on the steady-state mixing model of Robbins & Edgington (1975).

6.2.1. Profile KS1

KS1 is an interesting example of a profile in which the sedimentation and mixing rates have changed dramatically during the period to be dated. The annual varves in the uppermost 11.5 cm give an accurate time scale for that part of the core. In this layer the clear ^{137}Cs peak (1963) is at the expected place according to the deposition rate. Thus, the estimates of average sedimentation rates obtained by ^{137}Cs chronology and varve chronology for the period 1963–1981 are almost equal (Figs. 26 and 27). This result is in accordance with those reported by Jaakkola et al. (1983). In the varved sediments the effects of bioturbation and other mixing are minimal. Only slight migration of ^{137}Cs and ^{239,240}Pu can take place.

The ^{210}Pb concentration-depth curve of KS1 is not exponential. Hence, it is clear that the ages derived from the C.I.C. model are different from those of the C.R.S. model (Fig. 27). If the ages in the laminated layer are closer compared, it can be seen that the C.I.C. model ages are in agreement with the varve chronology, while the C.R.S. model ages (1957–1981) in contrast differ strikingly from the ages derived by the varve chronology, being significantly older than expected. Below the varved layer, where the ^{210}Pb does not follow the exponential curve, the C.I.C. model gives incorrect ages due to the 'kinked' form of the curve between 11.5–25 cm (Fig. 24). The C.R.S. model indicates a markedly higher sedimentation rate in this layer than in the varved layer and at the base of the core (Figs. 26 and 27).

It is probable that the flux of ^{210}Pb has remained constant at site KS1. The flux and total cumulative residuals of unsupported ^{210}Pb content are of the same order as in VS1 and VS3. The deviations from the exponential concentration curve in the layer of 11.5–approx. 25 cm can derive from the changes in the sedimentation rate. There is additional evidence of this in the structure of the sediment (cf. p. 39). The C.R.S.-model should however, in this case give the correct ages. It seems probable, therefore, that one of the basic assumptions for the use of C.R.S.-model, i.e. that there are no post-depositional migrations of ^{210}Pb in the sediment column, is not valid in this case. The biostratigraphy of chironomids (Kansanen 1985) clearly indicates that the bottom fauna was abundant and active below

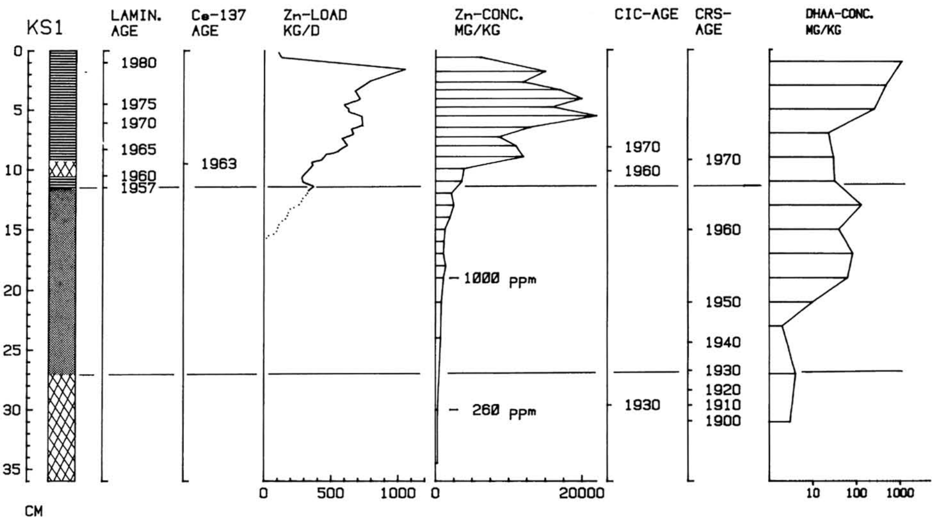


Fig. 27. Comparison of annual varve chronology ('lamin.age') with ^{137}Cs, C.I.C. and C.R.S. dating in profile KS1. Lithostratigraphy (for symbols, see Fig. 11). Zn and dehydroabietic acid contents are given, as well as the estimated Zn-load of industry in Valkeakoski. The Zn-load is given using varve chronology as a time scale. For the years 1943–1957 the time scale is based on the average sedimentation rate in the laminated layer.

the varved layer. Bioturbation is thus most likely the main reason for such migrations. A mixing layer in the ^{210}Pb-profile gives the impression of increased sedimentation (dilution). In many cases it is actually difficult to separate the effect of these two mechanisms (Jones & Bowser 1978).

In summary, profile KS1 can be divided into three main zones (Fig. 27):

I. From 36 cm to about 27 cm. No signs of oxygen depletion. A slight increase in zinc (cadmium, copper) from the background level commences, indicating the advent of cultural impact. The DHAA-content and a rising trend in the C-to-N ratio indicate the commencement of the impact of the waste-waters from the wood-processing industry. Zoobenthos is present, causing bioturbation (Kansanen 1985). No accurate age can be established for this zone. The C.I.C. ages are slightly younger than the C.R.S. ages. From the stratigraphic records and known loading history (Fig. 3) it can be roughly stated that the upper level of this zone represents the period 1920–1930 (rapid rise in industrial production). The lower layers may then have been deposited during the beginning of the industrial era at the end of the 19th century.

II. 27–11.5 cm. A rapidly increasing waste-water loading has caused periods of oxygen depletion during stagnation. This has also increased the sedimentation rate. The ^{210}Pb-profile, sediment structure, high DHAA-concentration and rise in the C-to-N ratio indicate direct sedimentation of the waste materials. At the same time the rate of bioturbation has probably increased (rise in the abundance of big *Chironomus*-larvae; Kansanen 1985). Accurate ages cannot be established due to the active particle reworking processes. The rise in zinc concentration to over 1000 mg/kg must be due to the advent of zinc loading from the rayon-fibre factory (commenced in 1943). The upper level represents the year 1957.

III. 11.5–0 cm. The water layers became almost permanently anoxic and the zoobenthos drastically decreased and totally vanished (Kansanen 1985). The preservation of the annual varves began in 1957. The zinc concentration follows the known history of Zn-loading rather well. The sedimentation rate has been variable, though on average lower than in zone II. A new boat route was dredged in 1960–61 and the waste-waters began to flow further to the south of site KS1. This is a probable reason for the phenomenon. The idea is supported by the decrease in DHAA-content and the drop in the C-to-N ratio at this level. The pH of the water fell owing to the acid waste-waters. This may explain the observed decrease in surficial Al and Cu concentrations, and partly also the decrease in Cd and Zn concentrations.

6.2.2. *Profiles VS1 and VS3*

VS1 and VS3 are examples of profiles in which there is clear evidence of surficial mixing (bioturbation). The exponentially decreasing ^{210}Pb concentration below the mixed layer reveals stable sedimentation conditions. It is unlikely that eutrophication or man's activities in the catchment area (land use) would have markedly increased the sedimentation rate in the large basin of Vanajanselkä. In large lakes the shoreline erosion of the basin itself, which is largely controlled by wind stress, is the most important mechanism in the formation of the source materials of deep-water sediments (Sly 1978, Edgington & Robbins 1979). In small basins or flow-through basins such as Kärjenniemenselkä the suspended matter of inflowing waters is clearly more important. Variations in the sedimentation rate caused by man's activities are therefore more probable in small basins than in Vanajanselkä.

Of the ^{210}Pb dating models the steady-state mixing model of Robbins & Edgington (1975) is most suitable for the observed profiles. The C.R.S. model interprets the low concentrations of the mixing layer as an increase in the sedimentation rate (Fig. 26). Below the mixed layer the derived sedimentation rate is lower than that calculated from the mixing model. This can be seen in Fig. 28. In the surficial layers the C.R.S. ages are slightly younger than the mixed model ages, but at the base of the core clearly older (only the years 1940-50 are at almost the same level). The time scale derived from C.R.S. in both profiles is misleading, especially in the lower part of the profile. Although the premises for the use of the C.I.C. model do not exist, the use of extrapolated surficial concentration gives a time scale roughly agreeing with that of the mixing model.

The sedimentation rate derived from the ^{239,240}Pu peak is markedly higher in both profiles than those obtained from ^{210}Pb dating (Fig. 26). According to the sedimentation rate obtained from the mixing model, the position of the 1963 maximum in fallout activity in VS1 should lie at 5.5 cm (the peak was at 9-10 cm) and in VS3 at 6.5 cm (9-10 cm) (Fig. 28). This indicates significant downward migration of ^{239,240}Pu and ^{137}Cs in both profiles. This phenomenon was reported by Robbins & Edgington (1975), and Robbins et al. (1977) from bioturbated sediments. The downward migration of the fallout peak resulted from the particle reworking in the mixing layer. It has been shown that in bioturbated sediments a peaked event will be vertically redistributed in the mixing layer. Due to the mixing the resulting concentration profile is not a normal distribution, but is more or less skewed, with a tail towards the sediment surface. The maximum concentration is at a lower level than expected. The transition downwards is dependent on the mixing activity and the rate of sedimentation. Excellent detailed presentations of the mixing process can be found in Guinasso & Schink (1975) and Schink & Guinasso (1977).

As pointed out by Håkanson & Källström (1978), the spread of particle bound materials in bioturbated sediments is often so significant that there is in fact no sense in giving a single age in years for a given sediment sequence. According to their calculations, the sediment layer of 12-13 cm in Lake Ekoln had a median age of 15.3 years, and the deposits from the median year only constituted about 15 % of the total amount of material in this particular layer. The age range of this layer was 22 years.

In this work the time resolution for profiles VS1 and VS3 (24.4 and 16.1 years) gives an impression of the smearing effect of bioturbation. In these cases it is only possible to establish average ages for the sediment layers. The steady-state mixing model only gives the mean sedimentation rate for the profiles and the age-depth distribution illustrated in Fig. 28 (mix. age) does not take into account the effect of particle reworking.

Nuclear fallout nuclides in the sediment can be considered as internal tracers with a distribution affected both by sedimentation rate and particle reworking. The maximum concentration of ^{137}Cs and ^{239,240}Pu represents a layer in which most of the material deposited in 1963 is concentrated. By comparing the levels of the year 1963 derived from ^{137}Cs (or ^{239,240}Pu) distribution and the steady-state mixing model, the downward transition (in cm) caused by bioturbation rate can be estimated. Assuming that the bioturbation and sedimentation rate have remained constant, and using the value of downward

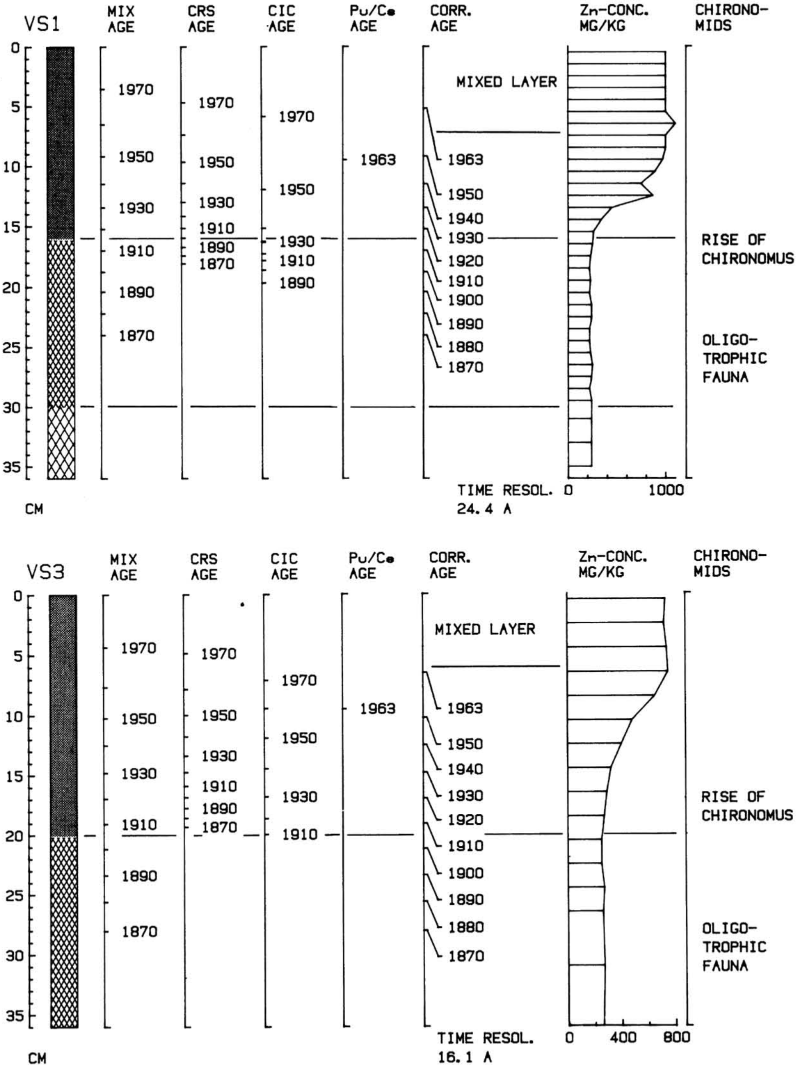


Fig. 28. Comparison of time scales derived from steady-state mixing model, C.R.S. model, C.I.C. model, artificial radionuclide chronology and corrected time scale ('corr. age') with Zn-stratigraphy and some events in the biostratigraphy of profiles VS1 and VS3 affected by heavy bioturbation (Kansanen 1985). For calculation of the corrected time scale see text. For lithostratigraphic symbols see Fig. 11.

transition (given as g/cm^2 dry matter to eliminate the effect of sediment compression) a corrected time scale can be presented (Fig. 28).

Fig. 28 shows that the corrected age scale is more in accordance with the zinc stratigraphy than the steady-state mixing model ages. Zinc has been affected by the mixing process in the same way as the radioactive tracers. A rise in zinc concentration above the background level begins to occur during the 1940s. The same accordance exists with the known history of the chironomid fauna. The oligotrophic faunal type was present in 1926 (Järnefelt 1929). The stratigraphy of the midge fauna (Kansanen 1985) shows that oligotrophic components were still present at a depth corresponding to the 1920s in the corrected age scale of both VS1 and VS3, but that they vanished soon after that.

6.2.3. Profile RS2

Profile RS2 is an example of a core which is probably affected by sediment slumping. Site RS2 is located at the bottom of a canyon-like depression. The value of the bottom roughness index was 4.3. Although the bottom in the near vicinity of the coring place was even and no disturbances in the particle size analyses and core stratigraphy were noted, it is probable that sediment material may have slumped down from the slopes of the depression (max. slope 13 m/100 m). This kind of highly increased sediment focusing has been reported earlier, e.g. by Ludlam (1974) and Smith & Walton (1980). Both the total cumulative ^{137}Cs and unsupported ^{210}Pb contents are markedly higher than in other cores. Fig. 29 shows that the layer of elevated zinc concentration and the FeS-coloured layer are discernibly thicker than in other cores. The ^{137}Cs stratigraphy has no clear peak. This also reveals sediment slumping and heavy sediment mixing.

The C.R.S. ages in this profile are also too old (Fig. 29). The zinc stratigraphy shows that the C.I.C. ages are in better accordance with the loading history. The thickness of the FeS-coloured layer supports the C.I.C. dating because other cores indicate that the near-bottom water layers became temporarily anoxic, probably during the period 1910–1930 (cf. Figs. 27–29).

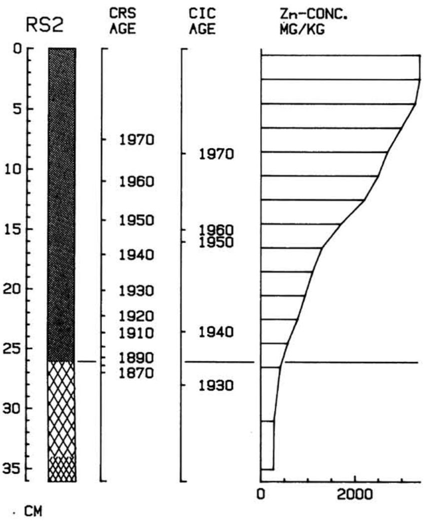


Fig. 29. Comparison of C.R.S. and C.I.C. dating models with zinc stratigraphy in profile RS2. For lithostratigraphic symbols see Fig. 11.

7. Concluding remarks

This work clearly demonstrates that there are several methodological difficulties and obvious limitations to be overcome before the historical information preserved in variable extent in lake sediments can be used in reliable environmental monitoring.

1. In large and complex lake basins unexpected current activity may occur in the deep-water area. Thus, attention must be paid to the selection of representative coring sites from accumulation bottoms. Preliminary mapping of surficial sediments by taking short cores (or echo-sounding) is necessary in evaluating recent bottom dynamic conditions.

2. Grain size in the sedimentary minerogenic matter can frequently be correlated to the integrated dynamic energy level. Grain size distribution parameters (standard deviation, skewness and kurtosis) can be the most useful sediment parameters indicating the processes of erosion, transportation and accumulation.

3. Even when the cores are taken from accumulation bottoms having a low dynamic energy level, mixing (bioturbation, gas formation or sediment slumping from steep bottom gradients) may partially obliterate the historical records in sediment layers.

4. The vertical distribution of artificial (^{137}Cs, ^{239,240}Pu) or natural (^{210}Pb) radionuclides can always be used to give information on prevailing sedimentation and mixing conditions at the given site. These distribution profiles give accurate ages in annually laminated sediments.

In the case of non-laminated sediments the effect of mixing must always be considered. It is preferable to use several alternative dating methods and to compare the results with 'local markers', if available.

— If particle reworking takes place in the sediment column, e.g. due to the bioturbation, it is possible to give only a certain mean age to every sediment slice, and the time resolution of historical events becomes low.

— In mixed profiles the dating results derived from the distribution of ^{210}Pb are strongly model dependent. The C.R.S. model will give logical, but misleading, mean ages. The C.I.C. model appears to be more useful than the C.R.S. model in these cases and it provides a rough idea of the mean age of sediment layers. — In bioturbated profiles, where the sedimentation rate can be assumed to be constant, the steady-state mixing model can give a reliable estimate of the sedimentation rate of the profile. The artificial nuclides acting as internal tracers indicate the effect of mixing (redistribution and downward migration) on the peaked events. The most reliable mean age scale can be achieved by combining the information from ^{210}Pb and artificial nuclides.

5. A specific pollutant such as zinc can be used as a tracer indicating the geographical distribution of contaminated waste waters and giving background information needed in the dating of the profiles. Heavy metals such as zinc are ideal tracers, if they have a specific pollution source. Organic compounds such as resin acids can also be used, but degradation in the water column, and even in the surficial layers, must be taken into account.

6. The stratigraphy of organic matter, carbon, nitrogen and phosphorus reveals eutrophication in the latest stage of the development of Lake Vanajavesi. The results are not, however, easy to interpret. One of the major weaknesses of the sediment analyses in lake monitoring is that it is impossible to estimate the nutrient loads discharged to the lake and the corresponding nutrient levels in the water phase. The carbon-to-nitrogen ratio and sedimentary chlorophyll content are better indicators of eutrophication than organic matter or nutrient concentrations.

The most reliable interpretation of the pollution history of Lake Vanajavesi can be made when the information of the chemical indicators is integrated with that of the biostratigraphic evidence.

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References

Alhonen, P. 1979: The sedimentary record of the cultural eutrophication and pollution of lakes in Finland. — Arch. Hydrobiol. 86:13-26.

Allan, R. J. & Brunskill, G. J. 1977: Relative atomic variation (RAV) of elements in lake sediments: Lake Winnipeg and other Canadian lakes. — In: Golterman, H. L. (ed.), Interactions between sediments and fresh water: 108-120. Wageningen.

Appleby, P. & Oldfield, F. 1978: The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. — Catena 5:1-8.

Appleby, P. G., Oldfield, F., Thompson, R., Huttunen, P. & Tolonen, K. 1979: ^{210}Pb dating of annually laminated lake sediments from Finland. — Nature 280:53-55.

Appleby, P. G. & Oldfield, F. 1983: The assessment of ^{210}Pb data from sites with varying sediment accumulation rates. — Hydrobiologia 103:29-36.

Auer, V. 1924: Die postglaziale Geschichte des Vanajavesisees. — Commun. Inst. Quaestionum Forestalium Finlandiae 8:1-156.

Autio, M. & Nordberg, T. 1972: Vuosisata paperiteollisuutta I. — 296 p. Valkeakoski.

Axelsson, V. & Håkanson, L. 1971: Sambandet mellan kvicksilverförekomst och sedimentologisk miljö i Ekoln. Del 1. Målsättning och analysmetodik. — UNGI Rapport 11 (Naturgeogr. inst.):1-35.

Beach Erosion Board 1972: Waves in inland reservoirs. — Beach Erosion Board Corp of Engineers Technical Mem. 132 (Ref. Håkanson, L. & Jansson, M. 1983).

Brownlee, B., Fox, M. E., Strachan, W. M. J. & Joshi, S. R. 1977: Distribution of dehydroabietic acid in sediments adjacent to a kraft pulp and paper mill. — J. Fish. Res. Board Can. 34:838-843.

Bruland, K. W., Bertine, K., Koide, M. & Goldberg, E. D. 1974: History of metal pollution in southern California coastal zone. — Env. Sci. Technol. 8:425-432.

Cambray, R. S., Playford, K. & Lewis, G. N. J. 1982: Radioactive fallout in air and rain: results to end of 1981. — United Kingdom Atomic Energy Authority Harwell, AERE-R-10485.

Damiani, V. & Thomas, R. L. 1974: The surficial sediments of the big bay section of the Bay of Quinte, Lake Ontario. — Can. J. Earth Sci. 11:1562-1576.

Davis, R. B. 1974: Stratigraphic effects of tubificids in profundal lake sediments. — Limnol. Oceanogr. 19:466-488.

DeGroot, A. J., Zschuppe, K. H. & Salomons, W. 1982:

Standardization of methods of analysis for heavy metals in sediments. — Hydrobiologia 92:689-695.

Digerfeldt, G. 1972: The postglacial development of Lake Trummen. Regional vegetation history, water level changes and palaeolimnology. — Folia Limnol. Scand. 16:1-104.

Edgington, D. N. & Robbins, J. A. 1975: The behaviour of plutonium and other long-lived radionuclides in Lake Michigan. II. Patterns of deposition in the sediments. — In: IAEA, Impacts of nuclear release into the aquatic environment: 245-260.

—"— 1976: Patterns of deposition of natural and fallout radionuclides in the sediments of Lake Michigan and their relation to limnological processes. — In: Nriagu, J. Q. (ed.), Environmental biogeochemistry 2:705-729, Ann Arbor.

—"— 1979: Correspondence. — Env. Sci. Technol. 13:480-482.

Elonen, P. 1971: Particle-size analysis of soil. — Acta Agralia Fennica 122:1-122.

Erviö, R. 1965: Valkeakoski-Leteensuo. — Chartae Agrogeol. 21. — Ann. Agric. Fennicae 4 (Suppl. 1):1-56.

Fogg, G. E. & Belcher, J. H. 1961: Pigments from the bottom deposits of an English lake. — New Phytol. 60:129-138.

Folk, R. L. 1966: A review of grain-size parameters. — Sedimentology 6:73-93.

Folk, R. L. & Ward, W. C. 1957: Brazos River Bar: a study in the significance of grain size parameters. — J. Sediment. Petrol. 27:3-26.

Fox, M. E. 1977: Persistence of dissolved compounds in kraft pulp and paper mill effluent plumes. — J. Fish. Res. Board Can. 34:798-804.

Förstner, U. & Wittmann, G. T. W. 1979: Metal pollution in the aquatic environment. — 486 pp. Berlin-Heidelberg-New York.

Goldberg, E. D. 1963: Geochronology with Pb^{210}. — In: IAEA, Radioactive dating, Proc. Symp. Athens 19-23 Nov. 1962: 121-131.

Gorham, E., Lund, J. W. G., Sanger, J. E. & Dean, W. E. Jr. 1974: Some relationships between algal standing crop, water chemistry and sediment chemistry in the English lakes. — Limnol. Oceanogr. 19:601-617.

Granberg, K. 1972: The diatom successions in the recent sediments and the eutrophication of Ristiselkä, Lake Päijänne, Central Finland. — Aqua Fennica 1972:20-27.

Groth, P. 1971: Untersuchungen über einige Spurenelemente in Seen. — Arch. Hydrobiol. 68:305-375.

Guinasso, N. J. Jr. & Schink, D. R. 1975: Quantitative estimates of biological mixing in abyssal sediments. — J. Geophys. Res. 80:3032-3043.

Hakala, I. 1971: A new model of the Kajak bottom sampler and other improvements in the zoobenthos sampling technique. — Ann. Zool. Fennici 8:422-426.

Hansen, K. 1961: Lake types and lake sediments. — Verh. Int. Verein. Limnol. 14:285-290.

Hardy, E. P., Krey, P. W. & Volchok, H. L. 1973: Global inventory and distribution of fallout plutonium. — Nature 241:444-445.

Hargrave, B. T. & Kamp Nielsen, L. 1977: Accumulation of sedimentary organic matter at the base of steep bottom gradients. — In: Golterman, H. L. (ed.), Interactions between sediments and fresh water: 168-173, Wageningen.

Heino, A. 1979: The pattern of organic content and some heavy metals in the bottom sediments of Airisto, SW-Finland. — Publ. Inst. Geogr. Univ. Turkuensis 89:1-52.

Helsingin yliopiston limmologian laitos 1979: Valkeakosken alapuolisen vesistön pohjasedimentin tila keväällä 1978. — Manuscript. Dept. Limnol. Univ. Helsinki.

Hiltunen, T. & Kansanen, P. 1983a: Veden liikkeet ja sedimentaatio järvessä (Abstract). — XI Geofysiikan päivät Oulussa 10.-11.5.1983: 113-114, Oulu.

—"— 1983b: Deep water erosion bottoms and water movements in a lake. — Proc. XVIII General Assembly Int. Assoc. Phys. Sci. Ocean (IUGG/IAPSO) 15-27 Aug. 1983: 285, Hamburg.

Hinneri, S. 1974: Enrichment of elements, especially heavy metals in recent sediments of the freshwater reservoir of Uusikaupunki, SW coastland of Finland. — Ann. Univ. Turkuensis (Ser. a II) 56:1-30.

Hjulström, F. 1935: Studies of the morphological activity of rivers as illustrated by the River Fyris. — Bull. Geol. Inst. Uppsala 25:221-527.

Holmbom, B. & Lehtinen, K.-J. 1980: Acute toxicity to fish of kraft pulp mill waste waters. — Paperi ja Puu 62:673-684.

Huttunen, P. & Meriläinen, J. 1978: New freezing device providing large unmixed sediment samples from lakes. — Ann. Bot. Fennici 15:128-130.

Håkanson, L. 1977a: Sediments as indicators of contamination. Investigations in the four largest Swedish lakes. - SNV PM 839 NLU Rapport 92:1-159.

—"— 1977b: The influence of wind, fetch and water depth on the distribution of sediments in Lake Vänern, Sweden. — Can. J. Earth Sci. 14:397-412.

—"— 1981a: Sjösedimenten i recipientkontrollen; principer, processer och praktiska exempel (Summary: Lake sediments in aquatic pollution control programs; principles, processes and practical examples). — SNV PM Rapport 1398:1-242.

—"— 1981b: Determination of characteristic values for physical and chemical lake parameters. — Water Resources Res. 17:1625-1640.

—"— 1981c: On lake bottom dynamics — the energy-topography factor. — Can. J. Earth Sci. 18:899-909.

—"— 1982: Bottom dynamics in lakes. — Hydrobiologia 91:9-22.

Håkanson, L. & Jansson, M. 1983: Principles of lake sedimentology. —316 pp. Berlin-Heidelberg-New York-Tokyo.

Håkanson, L. & Källström, A. 1978: An equation of state for biologically active lake sediments and its implications for interpretations of sediment data. — Sedimentology 25:205-226.

Institute of Radiation Protection 1982: Studies on environmental radioactivity in Finland 1981. — Annual Rep. Inst. Radiation Protection STL-A40:25-44.

Jaakkola, T., Mussalo, H. & Tiainen, S. 1979: Plutonium in the Helsinki air during 1962-1977. — In: Radioactive foodchains in the subarctic environment, Contract EY-76-C-02-3011 A 003 of the US DOE, Final Rep., Sept. 1979 (paper no 99).

Jaakkola, T., Tolonen, K., Huttunen, P. & Leskinen, S. 1983: The use of fallout ^{137}Cs and ^{239,240}Pu for dating of lake sediments. — Hydrobiologia

103:15-19.

Jones, B. F. & Bowser, C. J. 1978: The mineralogy and related chemistry of lake sediments. — In: Lerman, A. (ed.), Lakes, chemistry, geology, physics: 179-235. Berlin.

Järnefelt, H. 1929: Zur Limnologie einiger Gewässer Finnlands VI. — Ann. Soc. 'Vanamo' 8:105-164.

Kahila, S. K. 1971: Raa'an mäntyöljyn saanto, laatu ja koostumus (Summary: Yield, quality and composition of crude tall oil). — Kemian teollisuus 28:745-756.

Kajosaari, E. 1964: Toimialueen hydrologian pääpiirteet. — Hämeen Vesiensuojeluyhdistyksen Julkaisuja 3:1-53.

Kansanen, P. H. 1981: Effects of heavy pollution on the zoobenthos in Lake Vanajavesi, southern Finland, with special reference to the meiozoobenthos. — Ann. Zool. Fennici 18:243-251.

—"— 1985: Assessment of pollution history from recent sediments in Lake Vanajavesi, southern Finland. II. Changes in the Chironomidae, Chaoboridae and Ceratopogonidae (Diptera) fauna. — Ann. Zool. Fennici 22:57-90.

Kansanen, P. H. & Aho, J. 1981: Changes in the macrozoobenthos associations of polluted Lake Vanajavesi, Southern Finland, over a period of 50 years. — Ann. Zool. Fennici 18:73-101.

Kemp, P. L. W., Thomas, R. L., Dell, C. I. & Jaquet, J.-M. 1976: Cultural impact on the geochemistry of sediments in Lake Erie. — J. Fish. Res. Board Can. 33:440-462.

Koivo, L. & Oravainen, R. 1982: Zinc in water and sediments of two Finnish lakes. — Hydrobiologia 91:155-160.

—"— 1983: Zn, P and ATP in the sediments of two lakes in South Finland. — Hydrobiologia 103:177-179.

Krishnaswami, S. & Lal, D. 1978: Radioactive limnochronology. — In: Lerman, A. (ed.), Lakes, chemistry, geology, physics: 153-177. Berlin.

Kukkonen, E. 1973: Sedimentation and typological development in the basin of the lake Lohjanjärvi, South Finland. — Geol. Survey Finland Bull. 261:1-67.

Lounamaa, J. 1956: Trace elements in plants growing wild on different rocks in Finland. A semiquantitative spectrographic survey. — Ann. Bot. Soc. 'Vanamo' 29:1-195.

Ludlam, S. D. 1974: Fayetteville Green Lake, New York. 6. The role of turbidity current in lake sedimentation. — Limnol. Oceanogr. 19:656-664.

Matisto, A. 1970: Geological map of Finland. — Prequaternary rocks. Sheet 2132, Valkeakoski.

Mellenius, S. G. 1789: Undersökning om Nyland och Tavastehus län II. — Diss. för Prof. P. A. Gadd in Åbo, 22 pp.

Mäenpää, R., Hynnnen, P. & Tikka, J. 1968: On the occurrence of abietic and pimaric acid type resin acids in the effluents of sulphite and sulphate pulp mills. — Paperi ja Puu 4a:143-150.

Nienke, G. E. & Lee, F. F. 1982: Sorption of zinc by Lake Michigan sediments. Implications for zinc water quality criteria standards. — Water Res. 16:1373-1378.

Norrman, J. O. 1964: Lake Vättern. Investigations on shore and bottom morphology. — Geogr. Ann. 46:1-238.

Ohle, W. 1938: Die Bedeutung der Austauschvorgänge zwischen Schlamm und Wasser für den Stoffkreislauf der Gewässer. — Vom Wasser 13:87-97.

—"— 1963: Kolloidkomplexe als Kationen und Anionenaustauscher in Binnengewässern. — Vom Waser 30:50-64.

Oikari, A., Holmbom, B., Ånäs, E. & Bister, H. 1980: Distribution in recipient lake and bioaccumulation into fish of resin acids from kraft pulp mill waste waters. — Paperi ja Puu 4a:193-202.

Oikari, A., Holmbom, B. & Bister, H. 1982: Uptake of resin acids into tissues of trout (Salmo gairdneri Richardson). — Ann. Zool. Fennici 19:61-64.

Oldfield, F., Appleby, P. G. & Petit, D. 1980: A reevaluation of lead-210 chronology and the history of total lead influx in a small South Belgian pond. — Ambio 9:97-99.

Oravainen, R. 1977: Vuosiyhteenveto Vanajaveden ja Pyhäjärven vesistön yhteistarkkailusta vuodelta 1976. — Kokemäenjoen Vesistön Vesiensuojeluyhdistyksen Julkaisuja 75:1-47.

—"— 1978: Vuosiyhteenveto Vanajaveden-Pyhäjärven vesistön yhteistarkkailusta vuodelta 1977. — Kokemäenjoen Vesistön Vesiensuojeluyhdistyksen Julkaisuja 86:1-52.

—"— 1983: Vuosiyhteenveto Vanajaveden-Pyhäjärven vesistöalueen yhteistarkkailusta vuodelta 1982. — Kokemäenjoen Vesistön Vesiensuojeluyhdistyksen Julkaisuja 146:1-47.

Palander, L. P. 1767: Academisk afhandling och oekonomisk beskriftning ofver Kulsiala församling i Tavastehus län. — In: 1700-luvun Tyrväntöä aikalaisen silmin: 11-32, Hämeenlinna.

Palmén, E. G. 1903: Äldre och nyare sjöfällningar och sjöfällningsförsök i Finland. — Fennia 20:1-108.

Pasternak, K. 1974: The accumulation of heavy metals in the bottom sediments of the River Biala Przemscza as an indicator of their spreading by water courses from the centre of the zinc and lead mining and smelting industries. — Acta Hydrobiol. 16:51-63.

Pennington, W., Cambray, R.-S. & Fischer, E. M. 1973: Observations on lake sediments using fallout ^{137}Cs as a tracer. — Nature 242:324-326.

Rautalahti-Miettinen, E. 1977: Valkeakosken seudun jätevesien kulkeutuminen Vanajanselälle (Summary). — Nat. Board Waters Finland Rep. 135:1-63.

Ravera, O. & Parise, G. 1978: Eutrophication of Lake Lugano 'read' by means of planktonic remains in the sediment. — Schweiz. Zeitschr. Hydrol. 40:40-50.

Reineck, H.-E. & Singh, I. B. 1980: Depositional sedimentary environments. — 439 pp. Berlin-Heidelberg-New York.

Renberg, I. 1979: Environmental monitoring by chemical, physical and biological analyses of annually-laminated lake sediments — the possibilities of the method. — Nat. Swedish Environment Protection Board Rep. PM 1151:318-324.

Renberg, I. & Hellberg, T. 1982: The pH history of lakes in southwestern Sweden as calculated from the subfossil diatom flora of the sediments. — Ambio 11:30-33.

Robbins, J. A. 1978: Geochemical and geophysical applications of radioactive lead. — In: Nriagu, J. O. (ed.), The biogeochemistry of lead in the environment. Part A. Ecological cycles: 285-393. Amsterdam.

Robbins, J. A. 1982: Stratigraphic and dynamic effects of sediment reworking by Great Lakes zoobenthos. — Hydrobiologia 92:611-622.

Robbins, J. A. & Edgington, D. N. 1975: Determination of recent sedimentation rates in Lake Michigan using

Pb-210 ad Cs-137. — Geochimica Cosmochimica Acta 39:285-304.

Robbins, J. A., Krezoski, J. R. & Mozley, S. C. 1977: Radioactivity in sediments of Great Lakes: post depositional redistribution by deposit feeding organisms. — Earth Planet. Sci. Lett. 36:325-333.

Robbins, J. A., Edgington, D. N. & Kemp, A. L. W. 1978: Comparative lead-210, cesium-137 and pollen geochronologies of sediments from lakes Ontario and Erie. — Quatern. Res. 10:256-278.

Robbins, J. A., McCall, R. L., Fischer, J. B. & Krezoski, J. R. 1979: Effect of deposit feeders on migration of cesium-137 in lake sediments. — Earth Planet. Sci. Lett. 42:277-287.

Rosenqvist, J. Th. 1970: Formation of vivianite in holocene clay sediments. — Lithos 3:226-233.

Ryhänen, R. 1962: Über den Zustand der Gewässer im südlichen Einzugsgebiet des Kokemäenjoki (Finnland). III A. Ergebnisse der chemischen und physicalischen Winteruntersuchungen. — Ann. Acad. Sci. Fennicae (A III) 64:1-82.

—"— 1968: Die Bedeutung der Humussubstanzen im Stoffhaushalt der Gewässer Finnlands. — Verh. Int. Ver. Limnol. 14:168-178.

Saarnisto, M., Huttunen, P. & Tolonen, K. 1977: Annual lamination of sediments in Lake Lovojärvi, southern Finland, during the past 600 years. — Ann. Bot. Fennici 14:35-45.

Salkinoja, M., Saxelin, M.-L., Pere, J., Jaakkola, T., Saarikoski, J., Hakulinen, R. & Koistinen, O. 1981: Analysis of toxicity and biodegradability of organochlorine compounds released into the environment in bleaching effluents of kraft pulping. — In: Keith, L. H. (ed.), Advances in the identification and analysis of organic pollutants in water 2:1131-1164. Ann Arbor.

Salonen, K. 1971: Kokemäenjoen vesistön tarkkailu 1970, kasviplanktonin perustuotanto. — Kokemäenjoen Vesistön Vesiensuojeluyhdistyksen Julkaisuja 30:1-34.

—"— 1979: A versatile method for the rapid and accurate determination of carbon by high temperature combustion. — Limnol. Oceanogr. 24:177-183.

Sanger, J. E. & Gorham, E. 1972: Stratigraphy of fossil pigments as a guide to the postglacial history of Kirchner Marsh, Minnesota. — Limnol. Oceanogr. 17:840-854.

Schink, D. R. & Guinasso, N. L. Jr. 1977: Effects of bioturbation on sediment-seawater interaction. — Mar. Geol. 23:133-154.

Shepard, R. P. 1954: Nomenclature based on sand-silt-clay ratios. — J. Sedim. Petrol. 24:151-158.

Simola, E. F. 1903: Tiedonanto Leteensuon tutkimuksista Hattulan ja Kalvolan pitäjissä Hämeen lääniä. IV. Piirteitä Leteensuon historiasta. — Suomen Suoviljelysyhdistyksen Vuosikirja 1903:276-279.

Simola, H. 1977: Diatom succession in the formation of annually laminated sediment in Lovojärvi, a small eutrophicated lake. — Ann. Bot. Fennici 14:143-148.

—"— 1979: Micro-stratigraphy of sediment laminations deposited in a chemically stratifying eutrophic lake during the years 1913-1976. — Holarct. Ecol. 2:160-168.

—"— 1983: Limnological effects of peatland drainage and fertilization as reflected in the varved sediment of a deep lake. — Hydrobiologia 106:43-57.

Simola, H. & Tolonen, K. 1981: Diurnal laminations in the varved sediment of Lake Lovojärvi, South Finland. — Boreas 10:19-26.

Simola, K., Jaakkola, T., Miettinen, J. K., Niemistö, L. & Voipio, A. 1979: Vertical distribution of fallout plutonium in some sediment core from the Baltic Sea. — Finnish Mar. Res. 246:125-134.

Simola, L. 1963: Über die postglazialen Verhältnisse von Vanajavesi, Leteensuo und Lehijärvi sowie die Entwicklung ihrer Flora. — Ann. Acad. Sci. Fennicae (A III) 70:1-64.

Sly, P. G. 1977: Sedimentary environments in the Great Lakes. — In: Golterman, H. L. (ed.), Interactions between sediments and fresh water: 76-82. Wageningen.

—"— 1978: Sedimentary processes in lakes. — In: Lerman, A. (ed.), Lakes, chemistry, geology, physics: 65-89. Berlin.

Sly, P. G., Thomas, R. L. & Pelletier, B. R. 1982: Comparison of sediment energy-texture relationships in marine and lacustrine environments. — Hydrobiologia 91:71-84.

Smith, J. N. & Walton, A. 1980: Sediment accumulation rates and geochronologies measured in the Saquenay Fjord using the Pb-210 dating method. — Geochimica Cosmochimica Acta 44:225-240.

Solohub, J. T. & Klovan, J. E. 1970: Evaluation of grain-size parameters in lacustrine environments. — J. Sedim. Petrol. 40:81-101.

Sundborg, Å. 1956: The River Klarälven. A study of fluvial processes. — Geogr. Ann. 38:125-316.

Särkkä, J. & Paasivirta, L. 1972: Vertical distribution and abundance of the macro- and meiofauna in the profundal of Lake Päijänne, Finland. — Ann. Zool. Fennici 9:1-9.

Thomas, R. L., Kemp, A. L. W. & Lewis, C. F. M. 1972: Distribution, composition and characteristics of the surficial sediments of Lake Ontario. — J. Sedim. Petrol. 42:66-84.

—"— 1973: The surficial sediments of Lake Huron. — Can. J. Earth Sci. 10:226-265.

Thomas, R. L., Jaquet, J.-M. & Kemp, A. L. W. 1976: Surficial sediments of Lake Erie. — J. Fish. Res. Board Can. 33:385-403.

Tolonen, K. 1980a: Pollen, algal remains and macrosubfossils from lake Gallträsk, S. Finland. — Ann. Bot. Fennici 17:394-405.

—"— 1980b: Comparison between radiocarbon and varve dating in Lake Lampellonjärvi, South Finland. — Boreas 9:11-19.

Tolonen, K. & Jaakkola, T. 1983: History of lake acidification and air pollution studied on sediments in South Finland. — Ann. Bot. Fennici 20:57-78.

Tolonen, M. 1978: Palaeoecological studies on a small lake, S. Finland, with special emphasis on the history of land use. — Publ. Dept. Bot. Univ. Helsinki 4:1-8.

—"— 1979: On the prehistoric agriculture in Sääksmäki, S. Finland. — Finskt Museum 1976:67-84.

Uotila, P. 1971: Distribution and ecological features of hydrophytes in the polluted Lake Vanajavesi, S. Finland. — Ann. Bot. Fennici 8:257-295.

Vallentyne, J. R. 1955: Sedimentary chlorophyll determination as a palaeobotanical method. — Can. J. Bot. 33:304-313.

Wiederholm, T. & Eriksson, L. 1979: Subfossil chironomids as evidence of eutrophication in Ekoln Bay, central Sweden. — Hydrobiologia 62:195-208.

Williams, J. D. M., Jaquet, J.-M. & Thomas, R. L. 1976:

Forms of phosphorus in the surficial sediments of Lake Erie. — J. Fish. Res. Board Can. 33:413-429.
Wrenn, M. E. 1974: Environmental levels of plutonium and the transuranium elements. — In: Plutonium and other transuranium elements; Sources, environmental distribution and biomedical effects, U.S. Atomic Energy Commission Rep. WASH-1359:89.
Vuorela, I. 1980: Old organic material as a source of dating errors in sediments from Vanajavesi and its manifestation in the pollen stratigraphy. — Ann. Bot. Fennici 17:244-257.
Vuorinen, J. 1978: The influence of prior land use on the sediments of a small lake. — Pol. Arch. Hydrobiol. 25:443-451.

Appendix 1. Content of total and unsupported ^{210}Pb (mBq/g) and dry mass density (g dry matter/cm^3 fresh volume) in the sediment profiles of Lake Vanajavesi.

Profile/ depth (cm)	^{210}Pb Total	^{210}Pb Unsupp.	Dry mass density
KS1			
0.5	158.3	101.8	0.056
1.5	169.2	112.7	0.094
2.5	150.8	94.3	0.108
3.5	163.0	106.5	0.125
5.5	157.5	101.0	0.131
7.5	144.0	87.5	0.116
10.5	113.5	57.0	0.227
13.5	90.0	33.5	0.294
16.5	79.3	22.8	0.320
19.5	77.5	21.0	0.348
22.5	87.3	30.8	0.339
25.5	86.2	29.7	0.369
31.0	78.5	22.0	0.400
37.0	50.0	—	0.401
41.0	67.3	—	0.402
43.3	52.2	—	0.407
RS2			
0.5	175.8	133.0	0.057
1.5	189.7	145.5	0.122
2.5	187.5	143.3	0.146
3.5	171.7	127.5	0.129
4.5	181.2	137.0	0.172
5.5	172.5	128.3	0.180
7.5	173.0	128.8	0.219
9.5	154.0	109.8	0.246
11.5	145.5	101.3	0.254
13.5	137.5	93.3	0.273
15.5	118.8	74.7	0.306
17.5	95.0	50.8	0.293
19.5	90.7	46.5	0.308
21.5	91.0	46.8	0.346
24.5	100.0	55.8	0.298
27.5	77.3	31.8	0.259
31.0	46.3	—	
35.0	42.0	—	
VS1			
0.5	165.5	113.8	0.117
2.5	171.5	119.8	0.159
4.5	195.7	144.0	0.188
6.5	188.3	136.7	0.186
8.5	155.2	103.5	0.206
10.5	156.7	101.7	0.236
11.5	118.3	66.7	0.254
12.5	116.2	64.5	0.273
14.5	104.7	53.0	0.309
16.5	84.5	32.8	0.303
18.5	65.5	14.5	0.310
20.5	59.7	8.0	0.312
22.5	52.5	—	0.304
24.5	52.8	—	0.290
26.5	51.0	—	0.280
29.5	46.8	—	0.270
35.0	54.7	—	0.270
VS3			
0.5	199.8	144.5	0.113
1.5	174.5	119.2	0.136
3.5	181.0	125.7	0.188
5.5	178.2	122.8	0.200
7.5	166.3	111.0	0.228
9.5	140.5	85.2	0.301
11.5	121.4	66.2	0.303
14.5	101.2	45.8	0.322
17.5	85.5	30.2	0.331
19.5	66.2	10.8	0.343
20.5	69.8	14.5	0.326
23.5	55.9	—	0.319
25.5	55.6	—	0.302
29.5	55.7	—	0.267
37.0	54.0	—	0.300

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