

**Fig. 9.37.** Plot of ratio of light/(light+dark) laminae thickness from Lake Gościąg (thick line), in comparison with tree-ring widths of oaks from Koszalin (thin line) ( $t = 4.44$ ).

cation was connected with the settlement of village Dąb Borowy (Goslar, Chapter 9.2.1) in the near vicinity of the lake.

Some decrease of trophic is indicated at the depth of 76 cm (Figs 9.29 and 9.30) by a rise of Chrysophyceae concentration and decline of varve thickness, followed by an almost total extinction of vivianite in AD 1946. It might reflect the reduction of agricultural activity after farms were abandoned near the lake.

Short-term variations of laminae thickness were compared with those of tree-rings. For each varve, the sequences of thickness of light layer (i.e. that containing cysts, centric diatoms, and coarse calcite), dark layers (i.e. that of organic matter, deposited after calcite layer), light+dark, and the ratio of light/(light+dark) layers were compared with the sequences of tree-ring widths from 14 local oak chronologies from different regions of Poland (Ważny 1990, and pers. comm.). The correlation is reasonably dependent on geographical location of oaks (Fig. 9.36), showing the highest similarity of Gościąg sequences with those of oaks from the regions situated along the NW-SE transect of Poland. The best case of correlation is illustrated in Fig. 9.37. The documented positive correlations between tree-ring width and light/(light+dark) ratio as well as negative correlation between tree-ring width and organic varve thickness were the basis for searching for the correlation between the varve sequence from the Subboreal chronozone and the German oak chronologies (Goslar, Chapter 6.3). The mechanism linking tree-ring thickness and varve thickness parameters has not been resolved. According to Ważny (1990), the oaks in sequences from northern, western and eastern Poland respond positively to summer precipitation. The dependence of oak growth on temperature is less clear, e.g. the oaks

from northern Poland show significant positive response to the temperature of May, while those from eastern Poland seem to respond negatively to the temperature of June. The record of varve thickness was also compared with the instrumental records of monthly air temperature and the sum of precipitation, but no significant correlation was found.

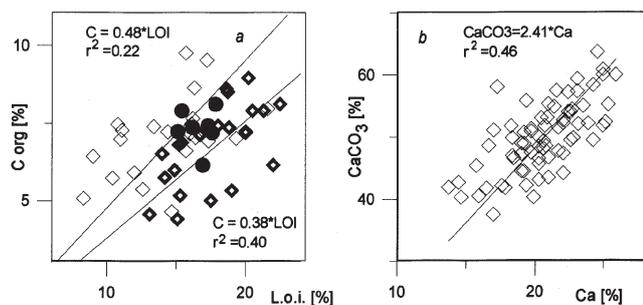
### 9.2.3. ANTHROPOGENIC CHANGES IN THE CHEMICAL COMPOSITION OF THE LAKE GOŚCIAŻ SEDIMENTS

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The seasonal variations of sediment composition, described in the previous section, were used to study the annual cycle and to construct the calendar chronology of sediments. Climatic and anthropogenic environmental variations are recorded in the sediment on a longer time basis. The composition of sediment may then reflect the human- and climate-driven changes of conditions in the lake catchment as well as in the lake itself. Here the time relationship between known anthropogenic events or climatic variations and the changes of chemical composition of sediment are presented.

In this study, the contents of organic matter, calcium carbonate, 14 elements, and accumulation rate were analysed.

For single varves between AD 1821 and 1955, the content of organic matter and carbonate was determined by the loss of sample mass during heating for 3h in 550°C (LOI = loss on ignition) and 900°C, respectively. The initial mass of dry sample was determined after heating in 130°C. In calculations it was assumed that all carbonate is that of calcium. The previous analyses, made on



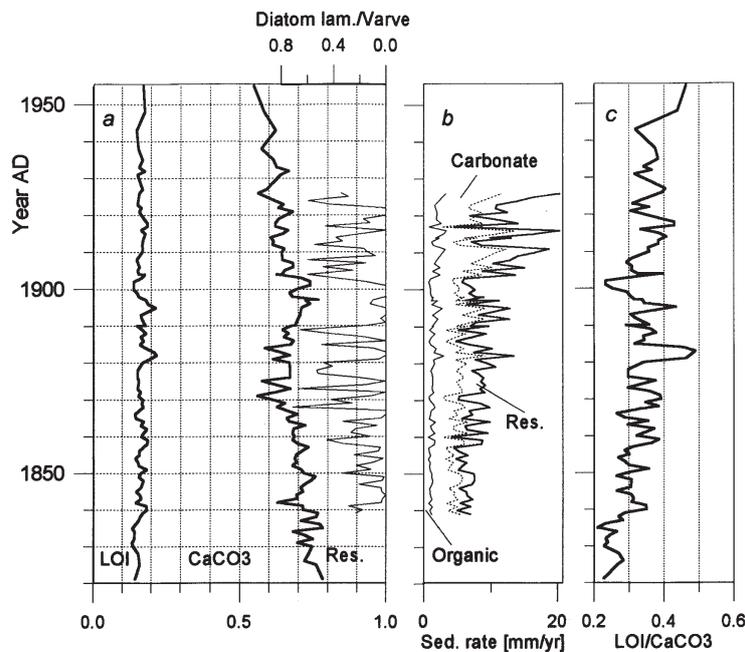
**Fig. 9.38.** Comparison of results of chemical and thermal analyses of the Lake Gościąż sediments. a – organic carbon content (C) versus loss on ignition (LOI). Diamonds – 10-yr samples from the whole profile of sediments: light diamonds – before 1000 cal BP; heavy diamonds – after 1000 cal BP; circles – single varve samples from the uppermost sediment. Organic carbon analyses were made by Łącka et al. (Chapter 8.2). b – correlation between CaCO<sub>3</sub> content determined by loss of mass in 900°C and Ca content in the uppermost sediments.

10 yr samples from the whole profile, demonstrated the correspondence between LOI (Wicik 1993) and organic carbon (Łącka et al., Chapter 7.3 and 8.2) which, before 1000 cal BP, constituted ca. 50% of LOI, although the correlation is not very high (Fig. 9.38a). The reasons for the weak correlation are difficult to explain. The successful modelling of apparent radiocarbon age of organic fraction of sediments (Goslar, Chapter 6.2), which used the organic carbon content derived from LOI, seems to suggest that the weak correlation between C and LOI results rather from imprecision of chemical than ignition

analyses. On the other hand, the deviation of model predictions in the last 1000 yr (Goslar, Chapter 6.2) could be explained by lower C/LOI ratio (ca. 40%, see Fig. 9.38a), suggesting real change of the ratio of organic carbon to organic matter after 1000 cal BP. Surprisingly, the ratio of organic C (Łącka et al., Chapter 8.2) to single-year LOI analyses presented here from 19th and 20th century, is similar to that observed in sediment prior to 1000 cal BP. The small year-to-year variation seems to prove that the precision of single-year LOI measurements was satisfactory (Fig. 9.39).

Much better correlation is that between Ca and ignition-calculated CaCO<sub>3</sub> content (Fig. 9.38b). The good stoichiometric correspondence between calcium and calcium carbonate proves the general reliability of results obtained by both methods. The spread of data around the linear relationship, however, is high. It might partly result from the fact that the sampling for both sets of analyses was done on different cores, and any sample of given varve could comprise not precisely defined admixture of material from adjacent varves. If this was the case, the correlation for three-year averages should be better than for single-year results. However, taking of three-year averages does not improve the correlation, so the most probable explanation of data spread is the imprecision of chemical analysis. Nevertheless, the general trends in carbonate (and calcium) content may be regarded as real.

The content of carbonate (Fig. 9.39a) reveals 10–20 yr fluctuations superimposed on a general decreasing trend between 60% and 40%. The fluctuations clearly coincide

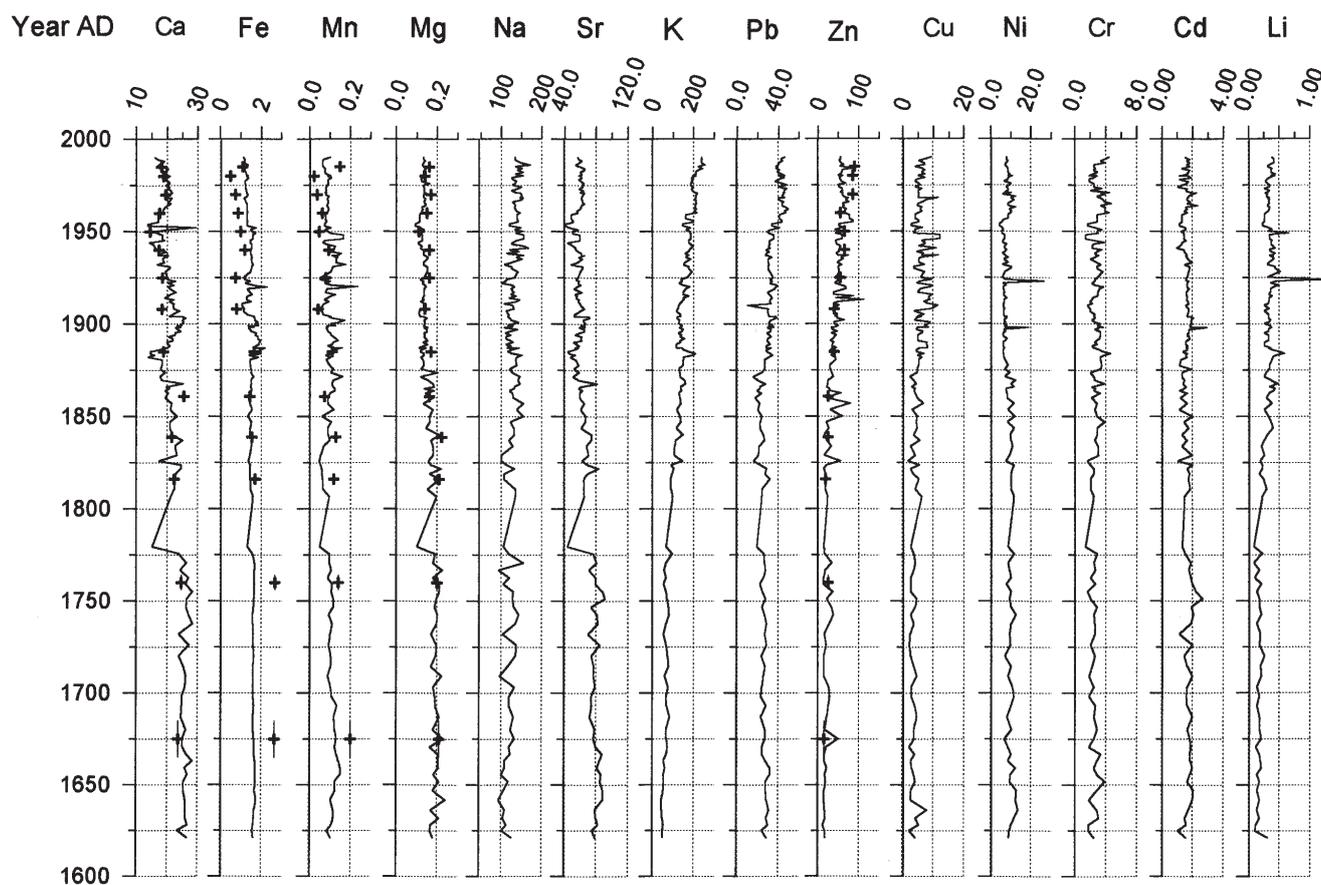


**Fig. 9.39.** Diagram of main sediment fractions and sedimentation rate of dominant components in the regularly laminated fragments of the youngest Lake Gościąż sediments. a – of organic matter (represented by LOI) and calcium carbonate content in the fragment of the Lake Gościąż sediments deposited between AD 1826 and AD 1955. The ratio of thickness of diatom laminae to whole varve is shown for comparison. b – accumulation rates of main sediment components in the fragment AD 1839/1926. c – ratio of LOI/CaCO<sub>3</sub> contents.

with those of diatom content. Distinct lowering between AD 1870 and 1880 was simultaneous with the presence of *Synedra* (see Chapter 9.2.2, Fig. 9.35), the high maximum of carbonate content about AD 1900, and a smaller one about AD 1920 coincide with the temporal extinctions of Centricae, while the lowering between AD 1905 and 1915 corresponds to the massive blooms of centric diatoms. It seems therefore that the residual matter is composed mostly of diatoms. Synchronous variations of sedimentation rates of three sediment components (Fig. 9.39b) suggest that they were controlled by a common factor, e.g. productivity of lacustrine biota. The relationship between calcite precipitation and organic productivity in the modern lake was evidenced by Wachniew and Rózański (Chapter 3.6). As demonstrated in Fig. 9.39c, the ratio of organic matter to carbonate between 1830 and 1950 increased by ca. 50%. The general trend of the LOI/CaCO<sub>3</sub> ratio could be an effect of decay of organic matter, which is faster than dissolution of carbonate. However, fairly constant content of organic matter with respect to total sediment over the whole period seems to exclude a diagenetic explanation. A decay hypothesis cannot also explain the coincidence between short-term variations of LOI/CaCO<sub>3</sub> and varve thickness. The ratio

of C+P+N/Ca, of meaning similar to LOI/CaCO<sub>3</sub>, was used by Tolonen (1978) as an indicator of trophicity of Lake Ahvenainen, Finland. She assumed that the increased sedimentation of these elements due to increased productivity cannot be eliminated by the correspondingly increased mineralisation of the sediment. In Gościąg sediment, both sedimentation rate and LOI/CaCO<sub>3</sub> ratio reveal minima in AD 1850–1860, about AD 1890, in AD 1895–1905, and about AD 1920, and maxima in AD 1880–1885, about AD 1893, and in AD 1910–1920. Such a coincidence, and the arguments presented above indicate that the observed changes in sedimentation rate and sediment content were driven mostly by varying biological productivity of the lake (including significant amounts of diatoms), which was followed by somewhat damped changes of precipitation of authigenic minerals.

The largest and most detailed record is that of elemental composition. The samples from the section of sediment for AD 1620–1881 encompassed 2–3 varves, and for AD 1882–1966 usually single varves were sampled. Because of no lamination, the boundaries between annual increments in the youngest section (AD 1967–1990) were not known. Therefore, the youngest section was divided into 24 fragments, assuming the exponential rise



**Fig. 9.40.** The records of content of 14 elements in the youngest 300 years of laminated sediments of Lake Gościąg. The contents of Ca, Fe, Mn, and Mg are given in per cent dry mass, the rest in ppm. The results of single analyses made by Łacka & Starnawska (crosses) are shown for comparison.

of accumulation rate. Each sample was dried out at room temperature and powdered, and 150 mg of dry sediment was used for further processing. The samples were treated with 1 ml 36% HCl, diluted to 10% with distilled water, and stored in 100°C for 1/2 h. Next distilled water was added to obtain 15 ml of solution, and the composition of the solvent was analysed by atomic absorption spectrometry. The analysed elements were: Ca, Fe, Mn, Mg, Na, K, Pb, Zn, Cu, Ni, Cr, Cd, and Li. The chemical pre-treatment and spectrometric analyses were done in the “Ekopomiar” laboratory by L. Chróst. This rather simplified procedure was chosen to minimize the number of steps that potentially might introduce additional spread of analytical results. It is suitable to study the changes rather than absolute concentrations, since the systematic error may be as high as a factor of two (Chróst, pers. comm.). Nevertheless, the comparison (Fig. 9.40) with the analyses of a few samples by more quantitative method (Łącka et al., Chapter 7.3 and 8.2), demonstrates reliability of results obtained.

The most abundant element is calcium, occurring as calcium carbonate. According to Łącka et al. (Chapters 7.3, 8.2) the other abundant elements are (in order of decreasing concentration): carbon (5–10%), iron (~5%), and silica (<5%). The other elements (including phosphorus, nitrogen, and sulphur) constitute less than 1% of sediment. Most components analysed here may be regarded as minor and trace elements.

The record of chemical sediment composition may be divided into three zones.

Zone A – ca. AD 1620–1780. This zone is characterized by rather constant chemical composition of sediment. Especially high with respect to the next zone are the contents of calcium and strontium. Other elements of high concentration are iron, manganese, and magnesium. Constant low concentration is revealed by potassium, lead, zinc, copper, and lithium. The separation of zone A in other elements is less distinct. The end of zone A is marked by a sharp minimum of nearly all analysed elements.

Zone B – AD 1780–1950. In this zone, the composition of sediment varies significantly. The general long-term increase is shown by potassium, lead, zinc, copper, and lithium. The increases of potassium and zinc are rather linear through the whole zone, while for lead, copper, and lithium the strongest increases occurred between ca. AD 1865 and ca. AD 1885. The concentrations of calcium, magnesium, strontium, and nickel decrease. Much less distinct is the decline of iron and manganese concentrations. Besides the long-term trend, calcium and strontium show also short-term variations, revealing distinct minima at AD 1880 and at the end of zone B and a maximum at AD 1905.

Zone C – AD 1950–1990. At the boundary between zone B and C the concentration of almost all elements

changes abruptly. Most distinct are the drops of iron, manganese, copper, and lithium, synchronous with increases of zinc and nickel. Less abrupt and somewhat delayed is the increase of calcium, strontium, potassium, lead, chromium, and cadmium. The trends of concentrations within this zone are rather weak.

The records in Fig. 9.40 show that certain groups of 14 elements have similar patterns of variations in concentration with time. Therefore their variability can be expressed with respect to principal components. Each principal component (PC) is a linear combination of 14 variables (concentrations) reflecting some specific pattern of similarity among element concentrations, and these combinations are orthogonal (i.e. not correlative) to one another. The coefficients of linear relationship between each PC and variables are called loadings. Then the composition of each sample is expressed by PC's. The principal component analysis was made by A. Walanus, using the program POLPAL, developed for palynological purposes. Prior to the calculation of principal components, the standard deviations of all variables were normalized to the same value. It appeared that 66% of total variance in the 14 transformed concentrations, might be expressed by only three principal components.

The loadings, and the records of three first PC's are shown in Fig. 9.41. The loadings demonstrate which element had the largest influence on creating the principal component. The sign of loading (positive or negative) represents the sign of the relationship between variable (element) and PC. The affinity of any variable to PC may be also expressed by the correlation coefficient between the record of the variable and that of principal component (Tab. 9.12).

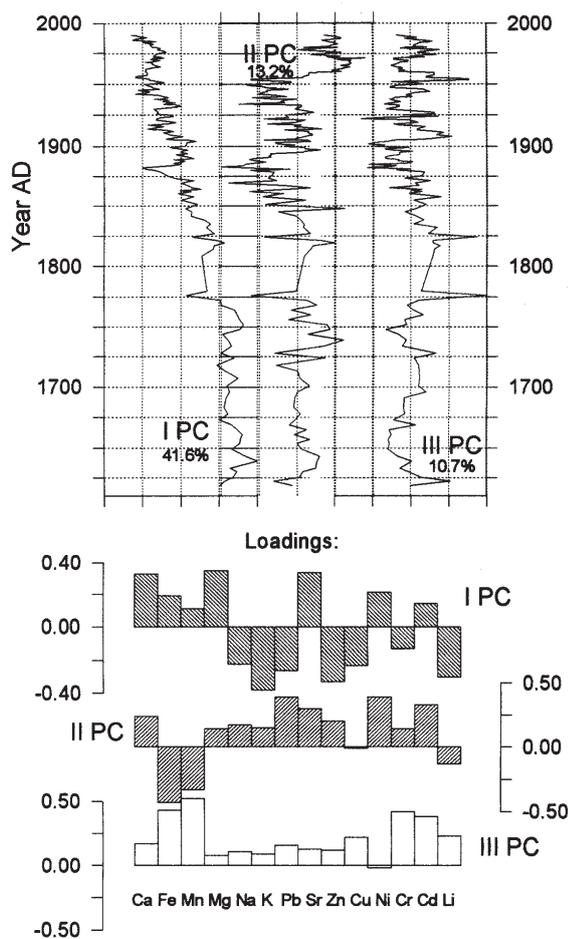
The first principal component (42% of total variance) is rather constant before ca. AD 1770 (zone A), declines

**Table 9.12.** Correlation coefficients between concentration of individual elements and three principal components. The coefficients higher than 0.5 are boldfaced.

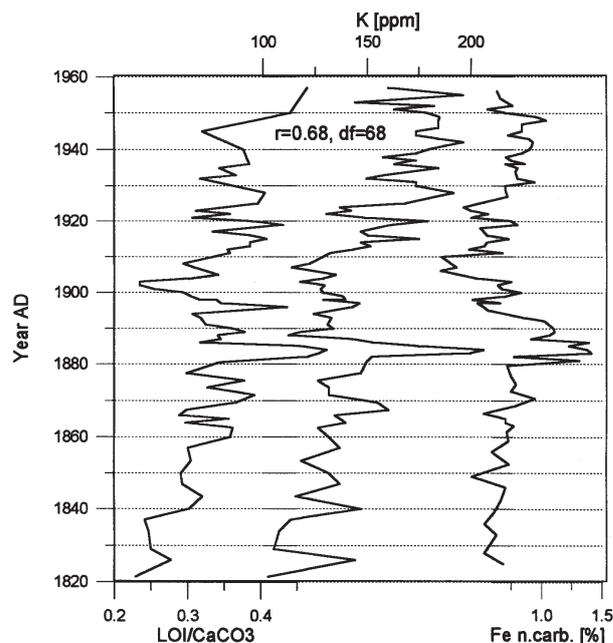
	I PC	II PC	III PC
Ca	<b>0.79</b>	0.31	0.20
Cr	-0.32	0.19	<b>0.51</b>
Cu	<b>-0.55</b>	0.01	0.29
Fe	0.46	<b>-0.58</b>	<b>0.53</b>
K	<b>-0.91</b>	0.22	0.11
Mg	<b>0.85</b>	0.18	0.09
Mn	0.22	-0.44	<b>0.67</b>
Na	<b>-0.54</b>	0.24	0.14
Ni	0.38	0.40	-0.02
Pb	<b>-0.61</b>	<b>0.50</b>	0.22
Sr	<b>0.83</b>	0.38	0.15
Zn	<b>-0.80</b>	0.24	0.10
Cd	0.32	0.42	0.45
Li	<b>-0.60</b>	-0.12	0.18

linearly in zone B (AD 1770–1955), and shows no general decline after AD 1955. The most important positive loadings to this PC are those of Ca, Mg, and Sr; the negative are K, Pb, Zn, and Li. Consequently the variations of the first PC are similar to the variations in concentration of most important positive loadings and similar to the inversed variations of negative loadings. The set of positive loadings is a consequence of high similarity of strontium and magnesium to calcium. This seems reasonable, since all these elements are usually bound in authigenic carbonates, though in some lakes, e.g. in Elk Lake, Minnesota, both magnesium and strontium appear to be associated with the clastic fraction (Dean 1993). The concentrations of iron and manganese are also positively correlated with the first PC. This might suggest that also some iron and manganese occur in form of carbonates. The proportion of loading suggests that iron and manganese carbonates constitute <5% and <1% of total carbonates, respectively. Such low concentrations are difficult to detect by X-ray diffraction, especially when they occur in the form of fine-grain fraction.

The highest negative loading to the first PC (and



**Fig. 9.41.** Plot of the first three principal components of content of 14 elements in the youngest 300-yr-long fragment of sediments of Lake Gościąż. Loadings of individual variables to each PC are shown below the plot.



**Fig. 9.42.** Plot of the LOI/CaCO<sub>3</sub> ratio, content of potassium, and content of the non-carbonate iron in the fragment of sediment of Lake Gościąż between AD 1821 and 1958.

correlation coefficient, see Tab. 9.12) is that of potassium, which shows nearly linear increase from ca. AD 1770 on. Potassium and other alkali elements occur in most lake sediments primarily in allogenic clastics eroded from catchment soils and rocks (Engstrom & Wright 1984). Therefore it is frequently interpreted as an indicator of erosion (Davis & Norton 1978, Tolonen 1978, Engstrom et al. 1991, Norton et al. 1992, Dean 1993). On the other hand, Michler et al. (1980), who reconstructed in detail the relationship between changes of concentrations of Na, Cu, and Mg in the sediment of Lake Ammersee, German Pre-Alps, and the change of area undergoing erosion in the lake catchment since Medieval time, could not find explanation for the permanent increase of potassium concentration. The increase of both K and Na concentration in recent years was attributed by Michler et al. (1980) to soil fertilization.

The concentration of potassium in the Lake Gościąż sediment is very well correlated with the ratio of organic to carbonate fraction (Fig. 9.42). As argued in former sections, that ratio is an indicator of biological lake productivity. Therefore the potassium in sediments of Lake Gościąż seems connected mostly with organic productivity of the lake. The onset of its increase about AD 1770 (Fig. 9.40) might be related to the “Hollandii” settlement, resulted in a split of “Dąb” settlements in the area (Goslar, Chapter 9.2.1). The distinct maximum at ca. AD 1883–1884 seems to be related to the settlement of Dąb Borowy and is delayed by 6–10 years with respect to the eutrophication suggested by the ratio of chrysophycean cysts to centric diatoms and other indicators (Goslar,

Chapter 9.2.1). The long-term rise of potassium content could be caused by the increasing crop of potatoes (fixing large amounts of that element) from the beginning of the 19th century on, and the gradual replacement of the three-year crop rotation by the shift of crops in land use. It appears that these changes were connected with enhanced soil fertilization. Mineral potassium fertilizers were introduced in the region only at the end of the 19th century (Goslar, Chapter 9.2.1).

The first principal component of 14 element concentrations reflects thus the decrease of carbonate content of sediment, related probably to the increasing lake productivity. The onset and termination of the decrease coincide with the development and abandoning of villages in the lake vicinity.

The second principal component (Fig. 9.41) remains rather constant below AD 1850, shows two broad minima in periods AD 1850–1890 and AD 1930–1955 and a large abrupt increase started in AD 1952 and completed before AD 1960. The II PC seems negatively correlated with the quality of lamination (see Goslar, Chapter 9.2.2, Fig. 9.33). The highest values of II PC occur in the non-laminated section, and the lowest values in the section AD 1825–1950, where the lamination was distinctly more regular than below. As shown by the loadings and correlation coefficients (Tab. 9.12) this PC reflects the opposition of iron and manganese with respect to other elements. Both iron and manganese are important paleolim-

nological indicators, and their geochemistry requires a more detailed discussion.

The iron and manganese can be found in lake sediments bound in the alloctogenic clastics and as components of authigenic oxides, sulfides, carbonates, and organic complexes. Authigenic forms of Fe and Mn are potentially labile, and their abundance in lake sediments is considerably dependent on post-depositional preservation. Thus the profiles of Fe and Mn are controlled by historical changes in both rate of supply to the lake and in processes controlling degree of preservation. The supply of these elements is a function of environmental processes occurring in the catchment, while preservation depends on conditions within the lake. The crucial point is that both elements exhibit very low solubility under oxidizing conditions, but under reducing conditions they may be released from the catchment soils as well as from lake sediments. Within the oxic regions, both elements exist in oxidized forms (Mn(IV), Fe(III)) as insoluble oxyhydroxides. In anoxic environments those elements are in their reduced forms (Mn(II), Fe(II)) and exist as mobile metal ions  $Mn^{2+}$  and  $Fe^{2+}$  (see e.g. Balistrieri et al. 1994). There are two important differences in the behaviour of Mn and Fe. First, Mn is more soluble than Fe, and it is first to be mobilized under oxygen depletion (Engstrom & Wright 1984). Second, Fe tends to be more involved in the sulphur cycle than Mn, and under extremely low redox potential, where  $H_2S$  is produced

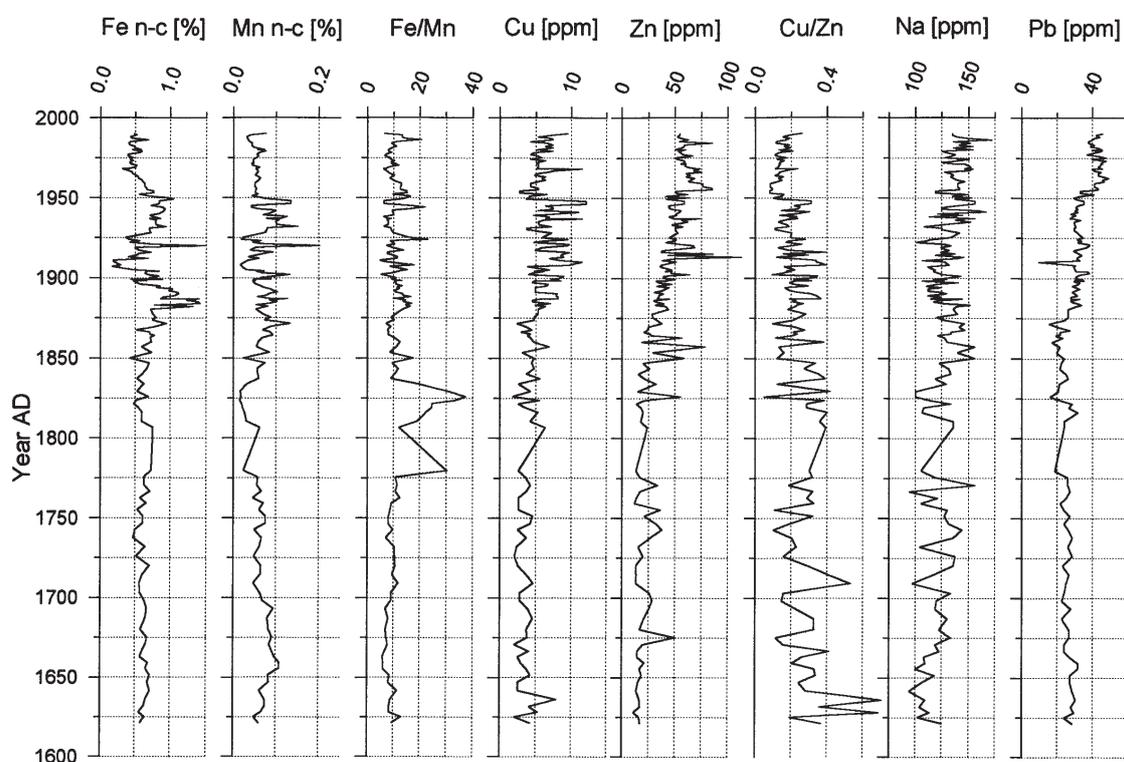


Fig. 9.43. Plot of the selected elemental content in the youngest fragment of sediments of Lake Gościąg. For iron and manganese the contents of non-carbonate forms are shown (see text).

through the decay of organic matter, it may precipitate in the form of very insoluble iron sulfides, FeS or FeS<sub>2</sub> (Wetzel 1975). Manganous sulfides, on the other hand, are much more soluble, and production of H<sub>2</sub>S does not inhibit dissolution of Mn from sediments (Engstrom & Wright 1984).

The effects of changing supply on Fe and Mn concentrations were demonstrated in studies of the post-glacial history of many lakes. In two Labrador lakes, Engstrom and Wright (1984) found marked increase of Fe and Mn concentrations coincident with the transition from tundra to coniferous forest in the drainage area. This change was interpreted as increased mobilization of both elements from the soils produced through the humus accumulation under conifer vegetation. Similar explanation was given by Dean (1993) for the high early-Holocene accumulation of Fe in Elk Lake, Minnesota. Mackereth (1966) hypothesized, that the differential mobility of Fe and Mn could be used to reconstruct redox conditions in catchment soils. He reasoned that the increase of the Fe/Mn ratio accompanied by the increase of Fe itself indicate lowering of redox in the surrounding soils. Such a change in the Lake Gościaż sediment at the Pleistocene/Holocene boundary (Łacka et al., Chapter 7.3; Goslar, Chapter 8.1) could thus be connected with the development of coniferous forests in the drainage area.

Beside its effect on mobilization of Fe and Mn from soils, the redox-solubility relationship is also important for the transport of these elements to lakes. Accordingly, both elements are transported to the lakes by oxygen-depleted groundwater, and the declines of Fe and Mn in sediment profiles from several Swedish and Norwegian lakes (Digerfeldt 1975, 1977) were explained by the progressive decrease in the flux of subsurface water.

The second, equally important factor controlling Fe and Mn profiles is the preservation in lake sediments. Iron and manganese, precipitated from the oxidized water column and accumulated in the sediments may easily be redissolved. In most lakes, only a thin uppermost layer of sediment is oxidized. The consumption of oxygen by microbial activity below that layer causes both Fe and Mn to be considerably more mobile and to enter into solution. They then may diffuse upwards and precipitate in the oxidized surface sediments. Such a migration results in Fe and Mn peaks at the top of sediment, which do not reflect the historical changes in sediment deposition (Engstrom & Wright 1984). The oxidized surface preserves these elements, once buried, from dissolution and escape back to the lake water. If hypolimnetic waters, and hence the uppermost sediments, become deoxygenated, the manganese, followed by iron, diffuse from the sediment into bottom waters. Such a mechanism is responsible for the hypolimnetic maxima of Fe and Mn concentrations near the water/sediment interface. In meromictic lakes, e.g. Hall Lake, Washington, USA (Balistrieri et al.

1994), such maxima seem to exist permanently. In seasonally stratified lakes, the hypolimnetic maxima are cancelled during overturn, and concentrations of both Fe and Mn rebuild above the sediment-water interface soon after stratification. In Elk Lake, Minnesota, the rebuilding takes a couple of weeks (Dean 1993), while according to Benoit & Hemond (1990) the total accumulated Fe and Mn may be dissolved even within a few days. In lakes like Elk Lake and Harvey's Lake, Vermont (Engstrom et al. 1985), both elements move many times between oxidized surface water and sediments before their loss from the system, either by final burial in sediments or by the flushing out of the lake.

Mackereth (1966) reasoned that in weakly anaerobic hypolimnia manganese, because of its greater mobility, could be selectively depleted in sediments, while under more severe anoxia both Fe and Mn will be lost. An additional separation of Mn from Fe may result from dissolution of Mn precipitates while they descend in anoxic waters (Davison 1981). Because of separation, the lowering of hypolimnetic redox should be reflected by peaks in the Fe/Mn ratio, coincident with minima in iron concentration.

Mayer et al. (1982) suggested that in some eutrophic lakes the release of Fe and Mn from sediments may be mediated by the formation of carbonates (siderite, rhodochrosite). Such a behaviour explains the correlation between Fe, Mn, and total carbonates, envisioned in IPC. Presumably a part of the observed variation of Fe and Mn is connected with the formation of carbonates. If we assume that the ratio of FeCO<sub>3</sub> and MnCO<sub>3</sub> to total carbonates was constant, we may calculate the concentration of both elements fixed in sediment in form of non-carbonate compounds. These concentrations (Fig. 9.43) do not reveal the long-term trend. Comparison of records in Figs 9.40 and 9.43 suggests that the carbonate compounds

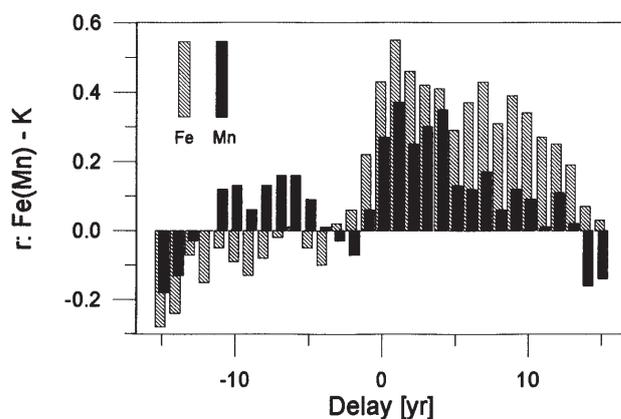


Fig. 9.44. Diagram showing the delay between changes of non-carbonate iron (and manganese) and potassium contents. The values of the correlation coefficient  $r$  are plotted as a function of shift of Fe (and Mn) versus K curves. Before calculations, long-term linear trend from the record of K content was removed.

constituted ca. 35–65% of total iron, and 20–50% of total manganese.

Having documented the changes of human presence in vicinity of Lake Gościąg (Goslar, Chapter 9.2.1) and changes of lamination quality (Goslar, Chapter 9.2.2), one would expect drastic changes in the concentration of accumulated iron and manganese. The variations of concentrations of both elements are well correlated but, surprisingly, the ratio of total as well as of non-carbonate Fe to Mn deposited in the Lake Gościąg sediments (Fig. 9.43) was more or less constant through the last 300 years. This would indicate that the redox potential in hypolimnion was usually low enough to inhibit the effects of changing separation between Mn and Fe. The only exception is the period AD 1800–1830 of the Fe/Mn maximum, coincident with minimum of Mn, and only minor lowering of Fe concentration. Palynological data suggests that most oaks were cut out at that time (Ralska-Jasiewiczowa & van Geel, Chapter 9.2.4), presumably used by the settlers of the developing “Dąb” villages (Goslar, Chapter 9.2.1). The maximum of Fe/Mn could thus be explained by temporal opening of forests, which caused the short-lasting soil oxidation and inhibited mobilization, especially of Mn, from the catchment soils.

The striking feature is an abrupt drop of Fe and Mn concentrations in AD 1953 (with no change of Fe/Mn ratio), 9 years after farms were abandoned near the lake (Goslar, Chapter 9.2.1). The drop of non-carbonate Fe is followed by the gradual decrease until AD 1967, coincident with the extinction of lamination after AD 1966. It is important that in the sediment deposited after AD 1966 not only calcite laminae are lacking but also diatoms and chrysophycean cysts do not form clear layers, which precludes the responsibility of post-depositional chemical processes, i.e. dissolution of calcite, for the observed lack of lamination. Another possible mechanism is mechanical disturbance, either by benthic fauna or wind-driven water movements. However, the abundance of benthic fauna in the present lake (Żbikowski 1993) is too low to produce appreciable disturbance of sediment (Giziński, pers. comm.). On the other hand, the occasional vertical circulation reaching lake bottom is documented by the profiles of temperature (see Fig. 3.6, Churski, Chapter 3.3). Such circulation could disrupt lamination not only by direct mixing in situ but also through the well documented (Giziński et al., Chapter 3.5) resuspension of sediments from shallower parts of the lake. Nevertheless, as documented by the presence of a few dispersed layers and by the well defined bomb-peak of  $^{14}\text{C}$  (Goslar et al. 1994), both mixing and resuspension could not affect the sediment deeper than a few centimeters.

Both the drop of Fe and Mn and extinction of lamination could result from abandoning of farms and consequent lowering of lake trophy in AD 1940–1946, suggested by Goslar (Chapter 9.2.2). The enhanced organic

productivity and more intense decay of organic matter in the upper sediment could increase the density of bottom waters, inhibiting the vertical circulation and decreasing the strength of spring and autumn overturns. Such a mechanism could explain the higher quality of lamination during periods of more intense human occupation in the last 3000 years (see Goslar, Chapter 8.2, Fig. 8.19), and also the appearance of regular lamination after development of “Dąb” villages at the beginning of the 19th century. If real, however, the circulation mechanism does not explain the observed drops of Fe and Mn concentrations by significant oxidation of sediment. The long-lasting oxidation should decrease the solubility, raise the concentrations of Fe and Mn, and also lower the Fe/Mn ratio. If, however, the redox potential increased at the very low level, it might inhibit formation of iron and manganese sulphides through the  $\text{H}_2\text{S}$ -involving mechanism and result in faster release of Fe from sediment. Such a mechanism should affect mostly iron, because the manganese sulphides are much more soluble.

The sulphide hypothesis explains the delay between changes of lake productivity and those of non-carbonate Fe concentrations, since decay of organic matter deposited proceeds through several years. Unfortunately, it cannot explain the abrupt drop of Fe in AD 1951 and especially the accompanying drop of Mn in AD 1949. An additional possible mechanism is that, driven by short-lasting circulation, replacement of Fe-Mn-rich hypolimnetic waters by the Fe-Mn-poor masses from lake surface would stimulate further diffusion of both dissolved elements from sediment. The Fe and Mn atoms would thus undergo more intense cycling between epilimnion and sediment before final burial, which of course increases probability of their loss from the lake with the outflowing water. Since manganese is more soluble than iron, increased circulation should be accompanied by an increase of Fe/Mn ratio. In fact, a small increase of the Fe/Mn ratio is observed.

Another paleoredox indicator is the ratio of copper to zinc concentrations. Vuorinen (1978) found that the decrease of redox potential of bottom waters from 100 mV to -200 mV was accompanied by an increase of Cu/Zn ratio from 0.1 to 0.4. In the Lake Gościąg sediments both elements tend to increase (perhaps due to increasing lake productivity) prior to AD 1949. Until AD 1948, the Cu/Zn ratio remained nearly constant, and in AD 1949 it dropped abruptly by a factor of two. Such a change seems to confirm slight oxidation of bottom waters, in accordance with the circulation hypothesis.

The drop of Fe concentration in AD 1951 is opposite to the increase in AD 1884 - 1887 following the lake eutrophication after settlement of Dąb Borowy. The delay of 7–13 years between the decline of trophy after abandoning the farms and the drop of Fe is similar to that between eutrophication after settlement of Dąb Borowy and

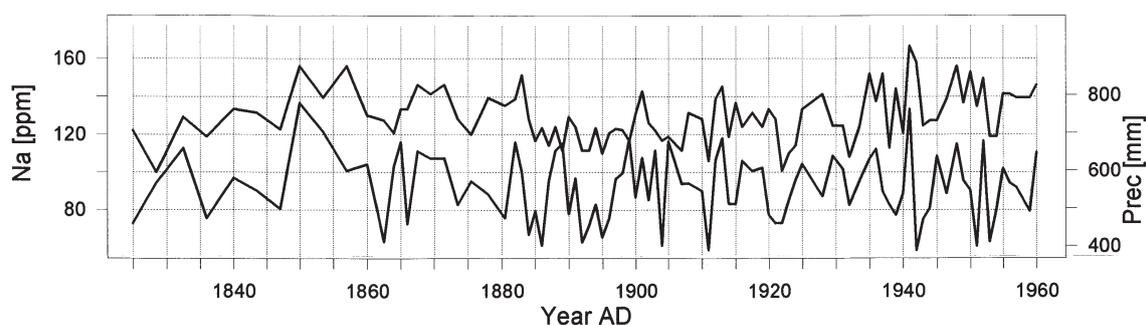


Fig. 9.45. Plot of the content of sodium in the sediment of Lake Gościąg, in comparison with the annual sum of precipitation.

rise of Fe lasting (depending on trophic indicator) 8–12 years. If the variations of Fe and Mn concentrations were driven by lake productivity through the sulphide or circulation mechanisms, they should be correlative with the indicators of organic productivity. As shown in Fig. 9.44, the variations of non-carbonate Fe and Mn concentrations show some delay with respect to the changes of potassium content (see Fig. 9.42). The asymmetry of correlation as a function of delay is reasonable, as the changes of organic productivity affect the rate of sulphide production in several following years but do not act back in time. Such a delayed correlation strongly confirms that the measured variations of element concentrations were not an artefact of simple interference with other elements (e.g. Ca) in the analytical process, but they document real dynamic ecological process.

Unlike potassium, iron, and manganese, all reflecting mostly human influence, the concentration of sodium seems to comprise the climatic information. This as well as potassium may be taken as an index of chemical weathering in the drainage basin and/or the erosive transport of soil particles to the lake (Engstrom & Wright 1984, Dean 1993). The concentration of sodium was compared with the mean annual sum of precipitation in Warsaw (ca. 100 km east of Lake Gościąg). The instrumental meteorological data were collected by S. Paczos and H. Maruszczak (Paczos 1993, Maruszczak 1988). In the analysed period AD 1825–1960, the Na concentration is significantly positively correlated with the annual sum of precipitation (Fig. 9.45), suggesting that the slope wash rather than chemical weathering is the main factor controlling the variations of Na content in lake sediment. The more detailed comparison, showing the weakest Na-precipitation dependence during summer season, when the soils are most stable against erosion, seems to support this interpretation. The concentration of potassium, however, is not correlative to precipitation. This was unexpected, since potassium undergoes less intense weathering and thus a stronger effect of erosion than sodium. As discussed earlier, similar behaviour of both elements was found in Lake Amersee in Germany (Michler et al. 1980).

The concentration of lead in the Lake Gościąg sediments (Fig. 9.43) increased first after AD 1880, and once again between AD 1950 and AD 1960. The lead concentrations in lake sediments were frequently used to study the effects of anthropogenic pollution (e.g. Renberg & Segerström 1981, Renberg 1986). The record from the Lake Gościąg sediments, however, seems seriously affected by the mobility of lead above AD 1950, clearly evidenced by the non-monotonic profile of  $^{210}\text{Pb}$  concentrations (Goslar, Chapter 9.2.2, Fig. 9.31). As discussed by Wachniew (1993), lead may be easily mobilized in reductive environments when the lack of sulphur inhibits fixation of Pb in form of sulphides. Therefore the profile of Pb in Gościąg, though it documents the increase after Second World War, is probably strongly flattened. Mobilization of lead in the upper part of the sediment of Lake Gościąg is concordant with effects explaining the Fe and Mn profiles.

The changes of other elements amounts are difficult to interpret. Those of Ni, Cd, and Li (Fig. 9.38) could reflect the industrial pollution by these metals; nevertheless, observed increases after AD 1960 are very low, perhaps because of situation of Lake Gościąg far from industrial centers.

#### 9.2.4. POLLEN RECORD OF ANTHROPOGENIC CHANGES OF VEGETATION IN THE LAKE GOŚCIAŻ REGION FROM AD 1660 UNTIL RECENT TIMES

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In the sediment cores from Lake Gościąg, obtained by means of piston corer, the quality of annual laminations deteriorates in the upper part of the sediment sequence until nearly total disappearance of laminae in the top 1.26 m. Thanks to the application of freezing *in situ* technique (Walanus, Chapter 4.1.2) the youngest part of sediment, except for its topmost ca. 50 cm, revealed also the existence of annual lamination, which enabled the construction of a continuous chronology based on correlation of laminae in 20 short frozen cores back to the middle of the 17th century (Goslar, Chapter 9.2.2). The new longest

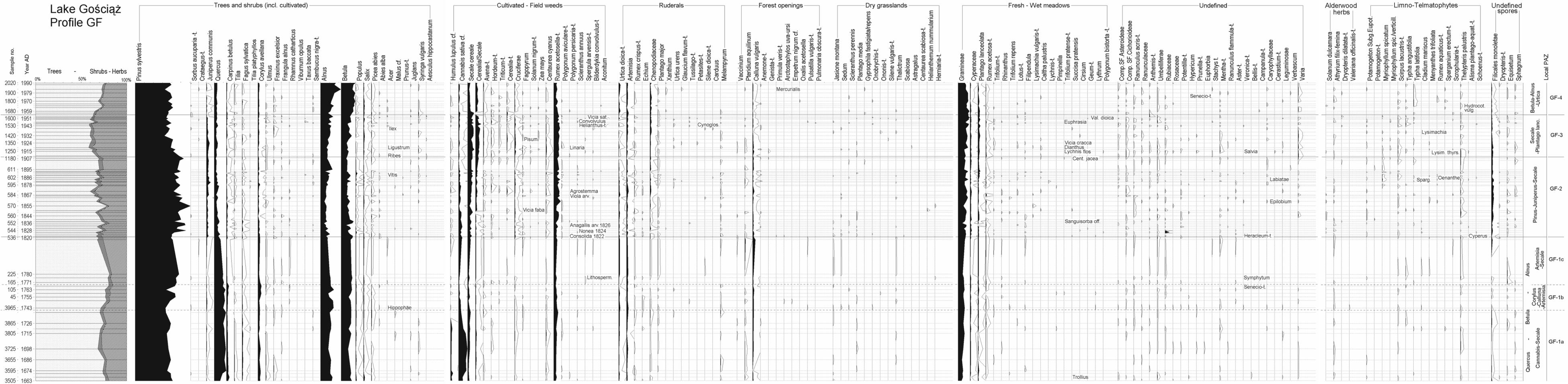


Fig. 9.46. Lake Gościąg, profile GF – percentage pollen diagram. The section of diagram drawn with contour lines cover the break in sampling sequence. The single pollen finds indicated by written names bear the date (year) of sample in places where the distances between sample levels were too narrow to write the taxon name in proper position.