

**Joanna Cieřlewicz**

**Chemistry of waters and bottom sediments  
in lakes with different  
catchment management**



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## List of abbreviations and symbols applied in the paper

- P1-P7 – symbols of field lakes  
L1-L7 – symbols of forest lakes  
PA – the symbol of sediment samples collected from the littoral zone of field lakes (the symbol used for humic acid samples)  
LA – the symbol of sediment samples collected from the littoral zone of forest lakes (the symbol used for humic acid samples)  
PB – the symbol of sediment samples collected from the profundal zone of field lakes (the symbol used for humic acid samples)  
LB – the symbol of sediment samples collected from the profundal zone of forest lakes (the symbol used for humic acid samples)  
TC – total carbon (in sediment samples)  
TOC – total organic carbon (in sediment samples)  
IC – inorganic carbon (in sediment samples)  
TN – total nitrogen (in sediment samples)  
HAs – humic acids  
 $A_{280}$ ,  $A_{400}$ ,  $A_{465}$ ,  $A_{600}$ ,  $A_{665}$  – absorbance of 1 cm layer of 0.003% HA solution in 0.05 M NaOH measured at the wavelength of 280 nm...665 nm, respectively  
 $A_{2/4}$  – the ratio of absorbance values of HA solutions (as above) measured at the wavelengths of 280 and 465 nm  
 $A_{2/6}$  – the ratio of absorbance values of HA solutions (as above) measured at the wavelengths of 280 and 665 nm  
 $A_{4/6}$  – the ratio of absorbance values of HA solutions (as above) measured at the wavelengths of 465 and 665 nm  
 $\Delta\log K$  – the difference in the values of logarithms for absorbance of HA solutions at the wavelengths of 400 and 600 nm ( $\Delta\log K = \log A_{400} - \log A_{600}$ ) [51]  
 $D4_{404}$  – the value of the fourth derivative of the standard spectrum of humic acids' solutions, multiplied by 1000 at the wavelength of 404 nm  
 $D4_{657-660}$  – the value of the fourth derivative of the standard spectrum of humic acids' solutions, multiplied by 1000 at the wavelength of 657-660 nm  
 $\omega$  – the state of internal oxidation of HA particles calculated on the basis of elemental composition according to the formula:  $\omega = (2O+3N-H)/C$  [97]



## FOREWORD

This paper presents the main problems related to functioning of lake ecosystems, as well as the research results, including characteristics of waters and bottom sediments of lakes with diverse management of a catchment area and the description of vegetation occurring in zones surrounding the reservoirs. For one should remember that a catchment area is a significant factor determining the physicochemical characteristics of lake waters and waters feeding the reservoirs. A characteristic feature of waters running off from the lowland forests is a high content of organic matter, slightly acid or acid reaction, and a relatively low content of nitrates(V). In forest streams on waterlogged soils, a high total content of free carbon dioxide and total iron is noteworthy, as well as a considerable content of orthophosphates(V). The waters running off from the agricultural catchment areas are characterized by a high content of nitrates(V) and the soil mineral and organic materials. The organic matter contained in waters and bottom sediments of lakes can originate from two different sources, from organisms living in a lake (autochthonous organic matter) and from substances that reach a lake from a catchment area (allochthonous organic matter). These two types of organic material differ from each other both in chemical composition and susceptibility to degradation. Organic material contained in sediments is diversified also within a reservoir, because vascular plants that contain cellulose and lignin are the main source of organic matter in the littoral zone, whereas phytoplankton is its main source in the pelagic zone.

Over time, under the influence of mechanical, biological and chemical factors, the bottom sediments deposited undergo certain internal transformations and consolidation. The processes of bottom sediment formation constitute an intrinsic link in the general process of transformations and circulation of the matter in aquatic environments. Therefore, they affect the chemical conditions and, to a large extent, also the life conditions prevailing in this environment. Bottom sediments of different water reservoirs are a product of not only the processes occurring in the aquatic environment, but also in the whole catchment area.

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# **1. INFLUENCE OF THE CATCHMENT AREA ON THE SURFACE WATERS AND BOTTOM SEDIMENTS**

A catchment area or a basin is defined as an area where all surface waters and ground waters gather and then drain off into a watercourse or a water reservoir. The area of the surface water runoff does not always coincide with the area of groundwater runoff. In the detailed discussions, both surface and underground catchment areas are distinguished.

Among hydrological factors defined as the hydrological regime of a river or a water reservoir – a basin clearly influences the natural retention of waters, feeding of watercourses and lakes with water, the variability of water levels and the water balance of surface waters. To a large extent, a catchment area determines also the morphology of river- and brook-beds, and also transformations of a basin of some lentic-water reservoirs. Consequently, through hydrological and chemical factors, a catchment area and particularly its substrate, significantly affects the colonization and life conditions of many aquatic organisms.

The nature of a catchment area is important both for the hydrological regime of the surface waters of all types and for the development of natural chemical composition of their waters and the occurrence (both in qualitative and quantitative terms) of the suspended matter and formation of bottom sediments. Chemical properties of the water in a catchment area are determined not only by its natural components, such as substrate and vegetation cover, but also by external factors – climate and human activity [80].

## **1.1. INFLUENCE OF THE FOREST ON THE AMOUNT AND QUALITY OF WATER RUNNING OFF FROM A CATCHMENT AREA**

Dense woody vegetation cover on the soil and the soil profile with a high content of organic matter in surface horizons influence both the climate and the water circulation, and at the same time the amount and quality of running off water. In dense forest areas, the air temperature is lower and the humidity is higher compared with open areas. The intensive turbulence with the airflow over the forest can accelerate the water vapour condensation and induce an increase in precipitation [4].

Not all the authors agree with the theory of favourable influence of forest on the amount of precipitation. Lambor [51] believes that this influence is limited to mountain and coastal areas, and furthermore, it is manifested during periods with the lowest water demand. There is, however, a consensus of opinions about the importance of forests for the water runoff and the water balance in forest areas. The year-long process of forest vegetation growth reduces the unproductive evaporation of an ecosystem as a whole, but it induces the increased evapotranspiration. Transpiration coefficients (the ratio of the amount of transpired water to the increase of dry matter) are lower for woody plants than for many cultivated plants. Values of this coefficient range from 299 for pine to 343 for oak, whereas for agricultural cultivated plants – the coefficient is higher than 400 [83].

The rainfall water passing through particular vegetation layers is subject to gradual retention. Interception of water in the crowns of trees depends on the species and foliage, as well as on the nature of precipitation. The average amount of water retained in the crowns of trees and in the undergrowth of oak-hornbeam forest ranges from 9.9% during the leafless season to 22.2% during the full-foliage season [43]. The water retained in tree crowns is not included in the runoff, but it is not known to what extent

all the vegetation layers can use this water, and at the same time reduce the transpiration. Reduction of the water uptake from the soil could consequently increase the water runoff. A relatively high amount of water can flow down the trunks of trees. According to Klein [43], during the growing season this amount reaches  $74.7 \text{ m}^3 \cdot \text{ha}^{-1}$ .

The fact of a slow temperature increase in the spring brings about the delayed snow-melt in forests. Due to the layer of litter and humified organic matter, the surface soil layer often does not freeze in winter, and thus the snow-melting water soaks into the soil and does not drain off its surface. The soil frost penetration depth in winter determines, inter alia, the size of the surface runoff during thawing [76]. According to the research by Kirwald [after 83], 100 mm precipitation soaked into the forest soil during 30 seconds, whereas into the meadow soil – during 3 hours. High porosity of forest soils causes that precipitation waters infiltrate quickly into the profile, which results in the reduction of surface runoff to almost zero. Greater surface runoff takes place only after torrential rains in catchment areas with a high slope. A characteristic feature of afforested catchment areas is underground feeding of streams, rivers and lakes.

Vegetation cover, soil and bedrock, which constitute an inseparable and mutually conditioned system in forest ecosystems, exert a strong influence on the chemical composition of running off waters. The specificity of this system is determined mainly by soils and soil processes, as well as underground water feeding of streams and rivers. Furthermore, during the process of washing through the tree crowns and flowing down along tree trunks, the properties of water are often modified before it reaches the soil. The water reaction after passing through crowns of pines in the Niepołomice Forest changes from  $\text{pH} = 5.6$  to  $\text{pH} = 4.5$  [93]. Water flowing down the tree stems is also subject to acidification, because the reaction of tree bark is often below the value of  $\text{pH} = 4.0$  [32].

Forest soils are characterized by accumulation of organic material on their surface. Inflow of organic matter during a year depends on the habitat type, species of trees and their age. In Central-European forests, it usually ranges within  $3.0\text{-}4.5 \text{ t} \cdot \text{ha}^{-1}$  (after [83]). Fallen leaves, needles, branches and other remains of forest vegetation go through the process of mineralization and humification. These two processes proceed in the surface soil layer. In the aerobic conditions and with neutral or slightly acid reaction, mineralization proceeds through rotting, as a result of which products of full oxidation are formed ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ) and mull-type humus develops. It is composed of water-insoluble humic acids, which are characterized by a high sorption capacity. Mull-type humus develops mainly in fertile habitats of deciduous forests [1]. Humus in the mull-type occurs in two – organic and humus – horizons. The organic horizon consists of the litter subhorizon (OI), which has a small thickness (sometimes discontinuous) and is built of slightly altered plant debris in the initial stage of transformation, usually derived from the last year's fall of above-ground plant parts, therefore it has the smallest thickness just before the autumn maximum. In the forest ecosystems with a high biological activity, the organic horizon may completely disappear already in the summer. A large fraction of the plant fall, which is brought there by soil animals, mainly earthworms, is decomposed in the humus horizon. The humus horizon of the mull humus type is well developed and very thick, grown through with roots of plants and characterized by large resources of humus [6, 69].

As in the mull type, humus in the moder type occurs mainly in organic and humic horizons, but differs in the development of these horizons. A few-centimetre thick

organic horizon is characterized by the occurrence of two subhorizons: litter (Ol) and detritus (Ofh). The litter subhorizon is composed of slightly transformed dead plant remains derived from the fall of above-ground plant parts from the last 2-3 years. In the detritus subhorizon, the material is older, highly fragmented and contains a considerable fraction of mineral material. The A horizon, with 10-15 cm thickness, contains on average 1.5-2% of humus. The genesis of this horizon involves mostly abundant, dying roots of herb-layer plants and small roots of trees [6].

In oligotrophic habitats of coniferous forests, with a considerable acidification of the environment, decomposition proceeds mainly with the contribution of fungi. The mor-type humus develops in such conditions, with a high content of water-soluble fulvic acids. High mobility of fulvic acids and their penetration deep into the soil profile, as well as the presence of soluble compounds of iron and aluminium, lead to fast podzolization of forest soils. In the conditions of a considerable acidification ( $\text{pH} < 5$ ), nitrifying bacteria do not develop, therefore ammonia ions are the main form of mineral nitrogen in the soils of coniferous-forest habitats [1]. Humus is accumulated in the well-developed and thicker organic horizon, in the poorly developed humus horizon, and also in the illuvial horizon. The organic horizon consists of three sub-horizons: litter (Ol), fermentation (Of) and epihumus (Oh). The litter subhorizon (Ol) is composed of small, altered plant-fall remains from the last 3-4 years, including easily recognisable needles, twigs, bark, cones and other components of the fall. The material is loosely assembled. In the fermentation subhorizon (Of), the material is highly fragmented and characterized by compact composition. Apart from highly decomposed plant remains, also excrements of small soil fauna and amorphous humus have a considerable contribution. The epihumic subhorizon (Oh) contains mainly macroscopically and microscopically amorphous humus. This subhorizon constitutes important reserves of nutrients for plants, which is evidenced by numerous small roots of plants present therein. Dying roots contribute in the development of this horizon. The humic horizon (A) with the thickness of 10-15 cm is grey in colour, which proves a small content of humus. The illuvial horizon (B) is often divided into two subhorizons: illuvial-humic (Bh) with a considerable content of humus and illuvial-ferruginous (Bfe), which is dominated by the accumulation of aluminium and iron [6, 69].

Soil types, types of forest humus, the structure of soil profile and the bedrock exert a strong influence on the chemical composition of water running off from forest area. This influence is stronger when the water circulation proceeds through the underground inflow. Due to a high diversity of forest habitats, it is not possible to explicitly determine their influence on the quality of running-off waters. One can say, however, that a high content of organic matter, slightly acid or acid reaction, as well as a relatively low content of nitrates(V) are the characteristic features of waters running off from lowland forests. It is noteworthy that the total content of free carbon and iron dioxides in forest streams is very high and is accompanied by a considerable content of phosphates.

For a number of reasons, the amount of basic nutrients that drain off from the forest soils is lower as compared with arable soils [10]. Forests usually occur on soils that are poorer in nutrients. Water runoff from under forests is lower than that in catchment areas under agricultural use. An important reason for a lower outflow of nutrients is the vegetation growth during the entire growing season and the continuous uptake of nutrients. Moreover, the multi-storey structure of root systems of the forest vegetation acts as a biological filter, preventing the migration of nutritional compounds.

## 1.2. INFLUENCE OF AGRICULTURAL LAND USE IN A CATCHMENT AREA ON THE SURFACE WATERS

The growth of population brought about an increased demand for food products, which resulted in an intensified agricultural production. The outflow of mineral components with crops considerably exceeds their inflow with organic fertilizers and crop residues, therefore it has become vital to supply the soil with minerals in the form of mineral fertilizers. As a result of the intensified agricultural production, the cycle of chemical elements in the system – fertilizers-soil-plant-crop – is characterized by a short time of nutrients' retention in the soil. Introduction of industrially produced mineral fertilizers for fertilization of soils increased the pool of nutrients in the biosphere. The increased animal production accelerated the circulation of the main chemical elements, and furthermore, switching to the so-called “industrial” breeding of farm animals contributed to a change in the direction of circulation of nutrients, since less of them return to soils, whereas more get to the water.

The inflow of municipal and industrial wastes and partially also those from large-herd breeding of animals is included within the so-called point sources of water pollution. The influence of agriculture becomes apparent mainly through the spatial inflow of nutrients into the surface waters. One should emphasize that the inflow of these compounds from agricultural areas consists of amounts that originate from soil elution and erosion, as well as runoffs from rural farms, while the latter ones should be considered as point sources.

Agriculture is based on plant production, which in turn is based mainly on cultivation of annual plants, which require ploughing and other agrotechnical procedures during the growing season. Furthermore, with cultivation of plants, depending on the species, the soil is devoid of vegetation cover during several weeks, or even months, during a year. The most drastic forms of human interference in basins of rivers and lakes is soil cultivation and long or short-term land fallowing. They mainly modify the water circulation in favour of surface runoff. On higher slopes, the maximum intensity of surface runoff on arable lands is up to several thousand times higher as compared with the water runoff in forest (Table 1). About a half of the surface runoff on arable lands proceeds via furrows and field roads.

Table 1. Surface runoff related to different land use [76]

Parameter	Meadow	Rye cultivation	Potato cultivation	Forest
Average slope inclination (%)	19	20	20	33
Maximum daily precipitation (mm)	48.4	48.4	48.4	70.3
Maximum daily runoff (mm)	24.4	15.3	21.4	0.02
Maximum daily runoff (%)	50.5	31.5	44.2	0
Maximum runoff intensity ( $\text{dm}^3 \cdot \text{min}^{-1} \cdot \text{ha}^{-1}$ )	565	668	3700	1

The water runoff velocity exceeds erosion velocity, therefore different soil fractions will be moved away with water. The degree of surface and concentrated washing away, which is called water erosion in agriculture, is very high at diversified lie of the catchment area. Gerlach [24] reports that on slopes with inclination of  $16^\circ$  and devoid of vegetation,  $63.2 \text{ t soil} \cdot \text{ha}^{-1}$  was washed away during the thawing season, whereas on slopes with a higher inclination ( $18^\circ$ ) but with the vegetation cover (green

fallow land), 10 times less of the soil material was moved away during the same time. Depending on the land relief, different amounts of material get into the surface waters, whereas the remaining amount is deposited at the slope foot. It is mainly the organic matter which is washed away together with eroded material. When the flood water rises, its content ranges from 7 to 16%, whereas when the flood water subsides – it ranges from 3 to 6% [23]. Humus losses in the eroded area are also confirmed by the recorded difference in the humus content in the soil material on the slope and at the base (0.59 and 4.83% respectively), which is typical of eroded fluvisols [96].

Water erosion is just one of the transport pathways of the soil material to surface waters, which is affected by agriculture. The second one – deflation (soil blowing) – is not less important in terms of soil degradation and the burden to waters. As a result of wind activity, soil particles smaller than 0.2 mm are transported as suspended matter, whereas fractions with a larger diameter are relocated by traction and saltation [48]. Contrary to water erosion, deflation is more selective, because the finest mineral fractions and humus are lost. The content of organic carbon in aeolian dust in northern Poland reached 17%, and nitrogen – 1.66% [30]. Deflation is a significant source of nitrogen and phosphorus compounds for surface waters. The most effective method for preventing water and air erosion is the permanent vegetation cover (long-lasting and alternating grasslands, winter crops, afforestation).

The catchment land use determines the leakage of dissolved substances to a lesser extent. Transport of compounds in the dissolved form is determined mainly by the amount of water in the surface runoff. The research on chemical erosion should comprise both the quantity of individual ions and their total quantity in the outflow from a catchment area, or in the inflow with precipitation.

The leaching of chemical compounds is determined mainly by fertility of soils, the amount of infiltrated water, as well as cultivated plants and phases of their development. The soil fertility, understood as a set of physical, chemical and biological factors which guarantee high production of ecosystems, is a broader concept than the soil nutrient availability, although it is often equated with the latter one. Mineral fertilization affects only one of the fertility factors, whereas organic fertilization contributes to an increased soil fertility, the improvement of the soil structure, an increased content of humus and soil sorption capacity, and also the activation of biological processes [54].

The content of main nutrients in the soil fluctuated within broad limits (Table 2), whereas almost total nitrogen occur in the organic form, potassium – only in the mineral form, phosphorus – in both forms. During the periods when soil is devoid of plants, more nutrients are leached from fertile soils, and also more nutrients are transported by the surface runoff [53].

Mobility and leaching of nutrients is determined by sorptive properties of soil. The content of nutrients in the water runoff from soils with low fertility is small, nevertheless with the intensification of plant production through mineral fertilization, less fertile, usually sandy soils lose more nutrients compared with more fertile and heavier soils. This is confirmed by studies conducted by Bartoszewicz [5] on the chemistry of ground water in agroecosystems. With a similar level of fertilization (300-350 kg NPK·ha<sup>-1</sup>), the highest concentrations of nitrates(V) reaching 100-120 mg N-NO<sub>3</sub><sup>-</sup>·dm<sup>-3</sup>, and occasionally 250 mg N-NO<sub>3</sub><sup>-</sup>·dm<sup>-3</sup>, were recorded in ground water of soil developed from sandy deposits. When analysing the relationship between the intensity of fertilization and the amount of nitrogen and phosphorus eluted from the soil in 63 different agroecosystems, Frissel [22] reported a high variability in the quantity of

eluted chemical elements. The amount of eluted nitrogen ranged from 1 to 90 kg N·ha<sup>-1</sup> per year. This variability was conditioned by the type of management – plant growing, animal breeding, the type of soil, the type of cultivated plants and agrotechnology. It was found that with rates not exceeding 150 kg N·ha<sup>-1</sup>, about 10% of nitrogen is washed out, with higher rates – ca. 20% of nitrogen supplied with fertilizers. Losses connected with volatilization of nitrogen, mainly in the form of ammonia, ranged from 2 to 90 kg N·ha<sup>-1</sup> per year. The amount of phosphorus eluted from soil was much lower (below 0,1 kg·ha<sup>-1</sup> per year) as compared with the amount lost via the surface runoff from eroded soils (mainly above 3 kg·ha<sup>-1</sup> per year) [75].

Table 2. The content of fertilizer components in the arable soil layer in Poland [26]

Component	g·kg <sup>-1</sup>	t·ha <sup>-1</sup>
Nitrogen	0.2-3.5	0.6-10.5
Phosphorus	0.1-2.0	0.3-6
Potassium	0.1-20.0	0.3-60
Calcium	0.7-36.0	2.1-108
Magnesium	0.6-12.0	1.8-36
Sulphur	0.02-1.2	0.06-3.6

### 1.3. INFLUENCE OF THE CATCHMENT AREA MANAGEMENT ON THE PROPERTIES OF BOTTOM SEDIMENTS

The primeval bottom of all water reservoirs, built of miscellaneous rock deposits, contains a certain amount of deposited autochthonous and allochthonous mineral-organic material. Alike inland soils, sediments of different aquatic environments are complex systems of crystalline and amorphous minerals of varying grain size with lower or higher content of organic matter, as well as mineral and organic colloidal substances. Autochthonous components of sediments are remains of plant and animal organisms inhabiting a specific aquatic environment, remains of undigested food and faeces of bigger animals, all falling to the bottom, dissolved and colloidal chemical compounds precipitating from the water, as well as materials that originate from abrasion of shores.

Allochthonous material consists mainly of products of catchment surface area erosion by rainfall water and wind, as well as washout of river beds. This group of sediment components comprises also contaminants that originate from production activity of man. The suspended matter of wastewater from industrial plants (coal and ore dressing, cellulose plants and others) and municipal sewage treatment plants are the largest source of anthropogenic material. Accumulation of sediments in water bodies is an irreversible geological process inevitably leading to their total disappearance, therefore inland reservoirs are the transitional landscape forms.

Bottom sediments of different water reservoirs are a product of the processes occurring not only in their environment, but also in the whole catchment area. Apart from surface erosion, among processes occurring in a basin, one can include landslides and complex mechanisms of transportation and accumulation of eroded materials. The process of sediment formation consists of three main stages: the development of substrate (erosion), the transport of the washed-out material and its sedimentation at the bottom.



Sedimentary processes, i.e. falling of the matter suspended in water down to the bottom under the force of gravity, take place in all aquatic environments. Not everywhere, however, they proceed in the same way and this is reflected in the spatial diversity of bottom sediments. The rate of sedimentation of solid particles is determined by properties of particles (size, volumetric density, shape) and characteristics of the sedimentation medium, including water movement intensity, density and viscosity. Sand grains are characterized by the fastest precipitation rate, whereas mineral colloidal fractions and fine organic particles – by the slowest one. Sedimentation velocity of suspension particles increases together with the temperature increase. Therefore, transport of suspension is easier in the winter-spring season compared with summer. Sedimentation is delayed by turbulence currents. Precipitation of particles in lentic waters is also significantly influenced by small plankton algae, which by developing on mineral particles can increase their weight and accelerate falling to the bottom, or increase their volume and prolong the precipitation time.

In all water reservoirs, sedimentation of suspended matter predominates over transport. In lakes, coarser mineral suspension supplied with the water inflow or created as a result of washed away shores does not spread far but accumulates near an inlet. The pelagic zone of lakes receives only the finest particles from the eroded allochthonous material. Horizontal diversification of sediments in lakes is conditioned not only by the spatial diversification of sedimentation of different-size mineral particles and by the runoff of sediments along the basin slopes into deeper zones, but also by qualitatively and quantitatively different inflows of organic particles related to zonal distribution of various groups of plants and animals. Because different groups of organisms constitute the source supplying the sediment with remains of organisms in the littoral zone, and yet another groups in the pelagic zone. In the littoral zone, macrophytes are the main source of slowly decomposing organic remains, and in the pelagic zone – plankton plants and animals, which due to fast mineralization only partially reach the bottom after their death.

The dominating amount and the quality of bottom sediments, characteristic of each reservoir, depends on the type and hydrological category of a reservoir (lakes, dam reservoirs, ponds), and within each category – on the trophic type of a given reservoir. The trophic type of a reservoir is determined mainly by the nature and the management of catchment areas (including mostly properties of the substrate, the relief and the surface area size), as well as by the morphology of a basin, which is connected with their genesis. The trophic type of a reservoir is reflected in a certain primary production volume, the content of biogenic elements in the water and in the bottom sediments, as well as in the content and stratification of oxygen. Each reservoir, from the very beginning of its existence, develops according to a characteristic “typological” line, determined by a catchment area. The main type of a reservoir, and at the same time the quality of sediments, can change only when a new radical factor (connected e.g. with the human activity) occurs within a catchment area. Among such drastic anthropogenic factors, one could list sewage discharge, changes in the catchment area management, as well as deforestation and turning the forest lands into cultivated lands, which results in the increased erosion [80].

## **2. LOCATION OF THE AREA AND THE RESEARCH SITES**

### **2.1. THE STUDY AREA**

Field studies were conducted in the former Piła Province. At present, the territories of this province are included in the Wielkopolska and West Pomerania Provinces. The studied lakes were situated within two macroregions – the South Pomeranian Lake District and the Wielkopolska Lake District.

#### **South Pomeranian Lake District**

The area of this macroregion (Fig. 1) amounts to 17,789 km<sup>2</sup>. The Lake District is situated outside the moraines of the Pomeranian phase, on the route of glaciofluvial water runoff, which built extensive outwash plains along the reaches of the Rivers Drawa, Gwda, Brda and Wda (Czarna Woda), which in turn disgorge into the ice-marginal valley of Noteć and Warta Rivers (Toruń-Eberswalde) and the Lower Vistula. In some places, moraine elevations jut out of the glaciofluvial sands. They are not that high as in the West Pomeranian or East Pomeranian Lake Districts. The climate of this region is drier and warmer compared with other lake districts, and pine dominates in the forest composition. The macroregion is divided into 12 mesoregions, which include i.a. the Szczecinek Lake District, the Krajna Lake District, the Wałcz Lake District, the Wałcz Plain and the Drawa Plain.

#### **Wielkopolska-Kujawy Lake District**

This macroregion (Fig. 1) of 15,700 km<sup>2</sup> is situated east of Zbąszyń Furrow, between the ice-marginal valleys of the Wisła, Noteć and Warta Rivers in the north and the Warta and Obra Rivers in the south. The land relief is associated with the occurrence of marginal and extraglacial forms from the Poznań phase of the Baltic Glaciation, as well as forms developed as a result of dead ice-melting at the end of the glacial period and in Holocene. The macroregion comprises 7 mesoregions, including the Chodzież Lake District.

The Chodzież Lake District, situated between the Noteć River Valley (the Toruń-Eberswald Ice-Marginal Valley) and the Wełna River Valley (a tributary of the Warta River), can be described as an agricultural region [44, 45].

### **2.2. RESEARCH SITES**

The research covered 14 lakes with diverse land use development in the direct catchment area. For most of the lakes, the catchment area was delimited based on 1:25000 maps. Lakes Strzałkowo, Murwinek, Zbyszewickie, Żońskie and Pawłowskie are located close to each other, therefore the total catchment area common to these lakes was quoted based on the Atlas of Polish Lakes [40]. Apart from the aforementioned lakes, the quoted area includes also the catchment area of Lakes Kaliszany, Oporzyńskie and Toniszewskie, which were not investigated. The soil types occurring in the lakes' catchment area were determined on the basis of 1:25000 maps made available by the Institute of Soil Science and Plant Cultivation in Puławy. Basic morphometric data of the studied lakes [3] are present in Table 3.



Fig. 1. Physical and geographical regions of the former Piła Province [47]

**Lake Bobrów (P1)** is located in the Wałcz Lake District (the West Pomerania Province), in the basin of Kłębowianka – Dobrzyca – Gwda – Noteć – Warta – Odra Rivers, at the altitude of 112.8 m asl. The lake waters are periodically fed by two drainage ditches, the outflow is located in the northern part. The direct catchment area of the lake with the area of 2.94 km<sup>2</sup> covers agricultural lands where Cambisols dominate. In the immediate vicinity of the lake, Histosols and Phaeozems occur fragmentary.

**Lake Murwinek (P2)** is a small water reservoir situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Dymnica – Rudka – Wełna – Warta – Odra Rivers, at the altitude of 87.4 m asl. From the north, the lake is connected with Lake Zbyszewickie and from the south – with Lake Strzałkowo.

**Lake Strzałkowo (P6)** is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Rudka – Wełna – Warta – Odra Rivers, at the altitude of 87 m asl [3]. From the north, the lake is connected with Lake Murwinek, whereas from the south – with Lake Kaliszany. Periodically the lake is fed by a drainage ditch.

**Lake Zbyszewickie (P3)** is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Dymnica – Rudka – Wełna – Warta – Odra Rivers, at the altitude of 90.0 m asl. The lake is connected with Lake Oporzyńskie in its northern part and with Lake Murwinek – in the southern part; the lake waters are fed by a ditch.

**Lake Pawłowskie (P4)** is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Rudka – Wełna – Warta – Odra Rivers, at the altitude of 97.6 m asl. In the north, the lake is connected with Lake Żońskie.

**Lake Żońskie (P7)** is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Dymnica – Rudka – Wełna – Warta – Odra Rivers, at the altitude of 87.8 m asl. In the south, the lake is connected with Lake Pawłowskie; the lake waters are fed by a drainage ditch.

The catchment area of Lakes Strzałkowo, Murwinek, Zbyszewickie, Pawłowskie and Żońskie, as well as Lakes Kaliszany Oporzyńskie and Toniszewskie not included in the research, comes to 63 km<sup>2</sup> and covers mostly agricultural lands. The catchment soils are built of Cambisols, proper Phaeozems and Arenosols.

**Lake Czeszewskie (P5)** is the largest one among the studied lakes. It is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Wełna – Warta – Odra Rivers, at the altitude of 90.1 m asl. In the east, the lake is connected by a channel with Lake Smuszewo. The basin with the area of 4.83 km<sup>2</sup> covers agricultural lands and wastelands. The soils occurring in the basin create a mosaic with the dominant contribution of Histosols. Cambisols and Phaeozems occur in the form of small patches.

**Lake Borowe (L5)** is located in the Drawa Plain (the West Pomerania Province), in the basin of Szczuczna – Drawa – Noteć – Warta – Odra Rivers, at the altitude of 43.9 m asl. It is an endorheic (with no outflow) lake, the basin with the area of 0.81 km<sup>2</sup> covers mainly forest lands (coniferous forests) on Cambisols.

**Lake Hanki (L4)** is located in the Wałcz Lake District (the West Pomerania Province) in the basin of Płociczna – Drawa – Noteć – Warta – Odra Rivers, at the altitude of 110.5 m asl. The catchment area of this endorheic lake comes to 0.69 km<sup>2</sup> and comprises lands covered mainly with coniferous forests occurring on Cambisols and Histosols.

**Lake Sumile (L3)** is located in the Wałcz Lake District (the West Pomerania Province), in the basin of Płytnica – Gwda – Noteć – Warta – Odra Rivers, at the altitude of 112.3 m asl. The lake is fed by a tributary situated in the south-western part, whereas the outflow is situated in the eastern part. The basin with the area of 0.59 km<sup>2</sup> comprises lands covered mainly with coniferous forests developed on Cambisols.

**Lake Czworokątne (L1)** is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Margoninka – Noteć – Warta – Odra Rivers, at the altitude of 65.8 m asl. The lake is connected with Lake Łabędź by a ditch situated in the western part. The direct catchment area of 0.43 km<sup>2</sup> is covered with deciduous and coniferous forests in ca. 80%, whereas agricultural lands constitute the remaining part. Cambisols are the main soil types in the catchment area.

**Lake Szamoty Duże (L6)** is situated in the Chodzież Lake District (the Wielkopolska Province), in the basin of Margoninka – Noteć – Warta – Odra Rivers, at the altitude of 66.7 m asl. It is an endorheic (with no outflow) lake with the basin of 0.24 km<sup>2</sup>, covered with deciduous and coniferous forests in ca. 75%, and with agricultural lands in the remaining part. Cambisols are the main soil types in the catchment area.

**Lake Krapsko Małe (L2)** is located in the Wałcz Plain (the West Pomerania Province), in the basin of Rurzyca – Płytnica – Dobrzyca – Gwda – Noteć – Warta – Odra Rivers, at the altitude of 85.3 m asl. The lake is fed by two tributaries located in the north-western part; the outflow is located in the south-eastern part. The basin with the area of 1.72 km<sup>2</sup> is covered with forests, mainly coniferous ones, occurring on Cambisols.

Table 3. Basic morphometric data of the studied lakes [3]

Lake	Total area (P) (ha)	Water surface area (ha)	Maximum depth (m)	Length (D) (m)	Width (S) (m)	Elongation (D/S)	The average width (P/D) (m)	Length of shores (m)
Bobrów	16.56	16.06	5.70	1120	200	5.60	169	2460
Murwinek	3.50	3.50	0.80	350	125	2.80	100	900
Zbyszewickie	37.04	34.54	7.20	1550	350	4.40	233	3475
Pawłowskie	17.40	17.40	5.25	950	260	3.70	183	2350
Czeszewskie	180.49	162.73	8.00	2600	820	3.20	571	6450
Strzałkowo	26.88	26.36	8.00	970	300	3.23	216	2664
Żońskie	24.10	24.10	7.00	1030	350	2.90	234	2600
Czworokątne	7.66	7.66	5.00	530	245	2.16	125	1375
Krapsko Małe	17.08	17.08	8.00	700	355	2.00	243	1795
Sumile	16.86	13.86	8.00	700	300	2.30	250	1825
Hanki	12.86	11.72	3.00	510	310	1.64	234	1420
Borowe	10.99	9.72	3.00	705	205	3.44	146	1740
Szamoty Duże	7.72	4.43	3.20	320	135	2.37	98	810
Pniewo	15.52	6.47	3.80	650	150	4.33	108	1940

**Lake Pniewo (L7)** is situated in the Szczecinek Lake District (the Wielkopolska Province), in the basin of Czarna – Gwda – Noteć – Warta – Odra Rivers, at the altitude of 131.1 m asl. The direct catchment area of 0.86 km<sup>2</sup> is covered mainly with coniferous forests growing on Cambisols [3, 14].

## **2.3. VEGETATION OF THE WATER RESERVOIRS AND THE ZONE SURROUNDING THE LAKES**

### **2.3.1. Ecological domains in the lakes**

Ecological domains develop as a result of different ecological factors operating both in the water column and at the bottom. The water column is divided horizontally into the neritic and inlake zone, i.e. the pelagic zone. Littoral, sublittoral and profundal zones are distinguished at the bottom.

The littoral zone comprises neritic waters above the bottom of the shore platform, and it reaches more or less down to the depth limit of macrophytes' occurrence [65]. Within *the littoral zone* one can distinguish 4 zones:

- epilittoral – the outermost area and entirely above the water,
- supralittoral – the spray zone,
- eulittoral – the proper shoreline zone, periodically flooded by water,
- infralittoral – permanently immersed bottom of a water reservoir within the occurrence range of macroflora [13].

*Sublittoral*, also called littoriprofundal, begins at the borderline where dense patches of underwater meadows end and the influence of waves ceases. It is a transitional zone, usually situated on the slope of the shore platform. Its lower range usually overlaps with the lower limit of metalimnion. A more accurate parameter determining the range of sublittoral is the nature of sediments, which develop within the sublittoral limits as a “heap” created from the littoral material and admixture of autogenic deposits, settling from the water column. The most typical sublittoral develops when the slope of the shore platform is steep.

The third bottom zone, *profundal*, is ecologically clearly defined. The bottom is covered with sediments of mostly organic and autochthonous origin [65].

### **2.3.2. Plant communities of water reservoirs**

Almost all groups of organisms are represented in the inland waters, ranging from bacteria to flowering plants, including monocotyledons that are particularly abundant. Aquatic flowering plants are classified within different taxonomic units, which indicates that their aquatic life style is a secondary adaptation, and thus all of them are of terrestrial origin. This theory is also supported by the fact that plants differ in the degree of their adaptation to life in the aquatic environment.

The nature and different extents of adaptation of vascular plants to life in the water, and in particular in the lake littoral zone, depends also on the prevailing conditions. The relief of the bottom surface, the nature and the amount of bottom sediments, water movement (wavy motion), physical properties of the water (transparency, thermal air currents) and its chemical properties (the quantity and the type of dissolved mineral salts) are important too. This is reflected in the zonal distribution of plants and indicates a different degree of their adaptation to aquatic environment.

Zonal distribution of vascular plants occurs in different inland water bodies, but it reaches full diversity only in lakes with high richness of plant forms. The following plant communities (phytocoenoses) are identified in the water:

**Amphiphytes** (Schröder, 1902). Amphibious plants, developing on the borderline between water and land, adapted to life both in water and on land. The zone of their occurrence runs along the peripheries, which are periodically under water.

Mosses from the following genera are typical representatives of this community: *Bryum*, *Calliergon*, *Drepanocladus*, *Sphagnum*; flowering plants, such as *Calla palustris*, *Alisma plantago-aquatica*, *Polygonum amphibium*, *Myriophyllum verticillatum* and others. The groups includes also hygrophilous plants, such as *Ranunculus reptans*, *Myosotis palustris* and a number of representatives from the genus *Carex*. Terrestrial and aquatic forms of *Riccia* can be encountered in this area.

**Helophytes** (Warming, Raunkiaer). Plants rooted in the bottom, with vegetative and fruiting shoots above the water surface. Two subgroups are distinguished in this group: reed beds and bulrushes.

**Reed beds** (Starmach, 1954). Plants occurring in shallow water, in marshy areas and temporarily under water, including helophytes adapted to periodic water flooding.

Mosses *Calliergon*, *Drepanocladus*, *Sphagnum* are represented here in great numbers, however species of *Carex* dominate, such as *Carex stricta*, *Carex gracilis*, *Carex lasiocarpa*, *Carex rostrata*, *Juncus compressus*, *Juncus articulatus*, *Heleocharis aciculari*, *Calla palustris*, *Acorus calamus* and a number of others. Their life is closely connected with aquatic environment, and in particular with lakes where they populate shallow and usually littoral waters.

**Bulrushes** (Starmach, 1954). Plants that develop in shallow littoral waters, and sometimes in inlake shoals. Bulrushes that grow at a certain distance from a shore on an offshore bar exposed to waves are called large-lake bulrushes [7, 9]. In sheltered places their range reaches a shore, and in waterlogged areas, they often grow on land.

Bulrushes are composed of a few species only, but they often occur in great quantities forming monospecies communities (aggregations). The common reed is the most typical and characteristic component of bulrushes, and among the emergent vegetation it occurs in the deepest parts of a lake (1.5-2.0 m). The species is strongly connected with the bottom by means of huge rhizomes and well developed roots. In the water, there are strong and highly lignified leafless stems, and above the water – leafy parts of plants with fruit and flowers rise. Leaves are attached to stems by means of long sheaths, as a consequence of which they change their position under the pressure of wind. It helps the common reed to resist blasts of wind and strong waves. Whereas the adaptation of *Schoenoplectus lacustris* and *Schoenoplectus Tabernaemontani* to strong wind and waves is of different nature. Elastic and flexible stems of these plants bend under the pressure of wind and waves. Therefore, they can develop not only along the windward shores, but also in shallow inlake waters of even extensive lakes.

*Equisetum limosum*, *Typha angustifolia*, *Typha latifolia* and other species develop in more sheltered places and on silted bottom.

**Nymphoides** (Du Rietz, 1921). Plants that develop on the bottom, with leaves floating on the water surface. Petioles of these plants are long, flexible and reach the water surface. Their strong and well developed rhizomes are deep in the bottom sediments protecting the plants from uprooting. They usually occur on the outer side of bulrushes in bays and sheltered places of lakes. Sometimes, however, they also occur among less dense bulrushes. They can occupy considerably large spaces displacing

other plant species, but only in small, sheltered and often confined lakes. All plants with floating leaves do not tolerate stronger water movements (rippling, water current) and sudden changes in the water level.

*Nuphar luteum*, *Nymphaea alba* and *Potamogeton natans* are typical representatives of this community. Furthermore, also *Nymphoides peltata*, *Polygonum amphibium* and *Nuphar pumilum* occur here.

**Elodeids** (Du Rietz, 1921). Plants are completely submerged in water, their assimilation and fruiting stems rise above the bottom but never grow above the water surface and do not form floating leaves, only flowers can jut out of the water. Plants of this community often form extensive underwater meadows, which constitute the lower storey of the littoral zone.

The species composition of this community comprises most of the species from the genus *Potamogeton*, and in particular *Potamogeton perfoliatus* commonly occurring in our waters, the biggest and the grandest *Potamogeton lucens*, as well as *Potamogeton pectinatus* and *Potamogeton crispus*. It also includes other plants occurring in large concentrations, such as *Batrachium circinatum*, *Ceratophyllum demersum*, *Myriophyllum spicatum* and *Elodea canadensis*.

**Isoetides** (Du Rietz, 1921). Plants that develop near the bottom and never reach the water surface. They usually form underwater turfs at shallow depths. The community covers larger areas only in some lakes. Those are usually relatively small vegetation patches on offshore bars.

Those are mainly low *Charales* (stoneworts), building for instance the association of *Charetum asparae*. The species composition of this community includes also *Isoetes lacustris*, which usually builds dense, monospecies patches. Moreover, different species of *Najas*, *Heleocharis acicularis* and *Litorelola uniflora* are encountered.

Isoetides develop on offshore bars of extensive lakes – usually in shallow waters between a shore and large-lake bulrushes, or in shallow inlake waters on the so-called underwater hills. Some plants of this community (*Isoetes lacustris*, *Najas*) can also occur in deeper places.

**Pleuston** (Schröder, 1902). Macroscopic plants, not rooted, but floating on the water surface or in the water. They do not form stable communities and often develop under the cover of rooted plants.

The following species occur in the composition of this community: *Ricciocarpus natans*, *Salvinia natans*, different species of *Utricularia*, *Aldrovanda vesiculosa*, *Hydrocharis morsus-rangae* and representatives of the family *Lamnaceae*. Pleuston includes also macroscopic algae floating on the water surface in the form of cottony aggregations composed mainly of the genera: *Hydrodictyon*, *Zygnema*, *Spirogyra*, *Cladophora* and others [8].

### 2.3.3. Plant communities of the zone directly surrounding the studied lakes

Vegetation of the ecotone zone (a zone immediately around a lake or a watercourse) is one of the factors determining the chemical composition and the amount of waters flowing into the water reservoirs and watercourses. Ecotone buffer zones can reduce the load of nutrients and mechanically retain mineral fractions coming from erosion. According to Gilliam and co-authors [25], the reduction can reach 88%. Denitrification is another important process. In the literature dealing with lakes in different parts of the United States, there are data confirming that 68-89% of nitrogen reaching the ecotone zones from a catchment area is removed in the process of denitrification [95].

Plant communities of the zone situated immediately around a lake were described using the phytosociological method. About 200 relevés were made using the method of Braun-Blanquet. Based on the collected material, plant communities were described and classified according to the Guide for identification of plant communities in Poland [57].

### Lake Bobrów

Fragmentary communities of reed beds occurred in the littoral zone. They were represented by *Ass. Phragmitetum communis* ((Gams 1927) Schmale 1939) and *Ass. Typhetum latifoliae* (Soó 1927), and *Ass. Nupharo-Nymphaetum albae* (Tomasz. 1977) characteristic of aquatic plant communities. Within the zone directly surrounding the lake, forest communities dominated, including *Ass. Circaeo-Alnetum* (Oberd. 1953), *Ass. Galio silvatici-Carpinetum* (Oberd. 1957) and *Ass. Tilio-Carpinetum* (Lose. 1962). Meadow communities represented by the meadow from the order of *Molinietalia* (*Ass. Epilobio-Juncetum effusi*; Oberd. 1957); tall herbaceous vegetation (*Ass. Filipendulo-Geraniatum*; Koch 1926) and *Ass. Geranio-Peucedanetum cervariae* ((Kuhn 1937) Müll. 1961) formed small patches; a large patch of meadows from the order of *Molinietalia* (*Ass. Cirsio-Polygonetum*; R. Tx. 1951) occurred only in the eastern part of the lake. Further on, the area was covered by vegetation of *Ass. Vicietum tetraspermae* ((Krussem. et Vlieg. 1939) Kornaś 1950) characteristic of field communities (Fig. 2) [14].

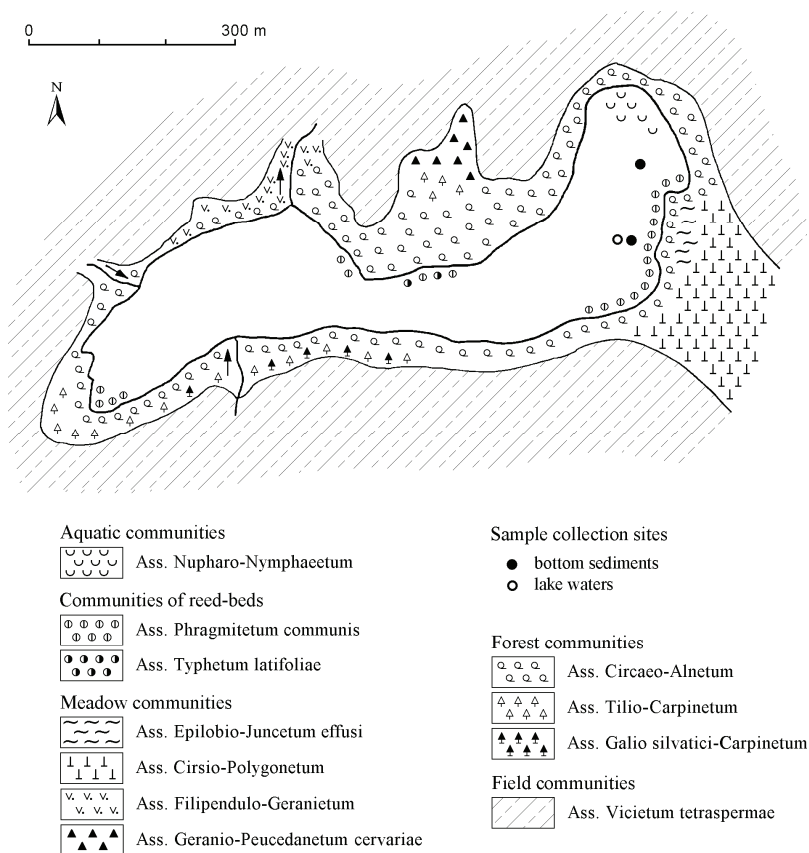


Fig. 2. Plant communities of the zone directly surrounding Lake Bobrów [14]



### Lake Murwinek

Communities of aquatic plants occurred in the littoral zone of the lake and they were represented by *Ass. Nupharo-Nymphaetum albae*, as well as reed and rush communities in the form of *Ass. Phragmitetum communis*, *Ass. Typhetum latifoliae* and *Ass. Acoretum calami* (Kobendza 1948). The lake was surrounded by numerous meadow communities represented by associations: meadows from the order *Magnocaricetalia* (*Ass. Caricetum acutiformis*; Sauer 1937), meadows from the order *Molinietalia* (*Ass. Epilobio-Juncetum effusi*), meadows from the order *Molinietalia* (*Ass. Cirsio-Polygonetum*), grazing lands from the order *Arrhenatheretalia* (*Ass. Lolio-Cynosuretum*; R. Tx. 1937) and the order of *Molinietalia* (*Ass. Junco-Molinietum*; Prsg 1951), tall herbaceous vegetation (*Ass. Filipendulo-Geraniatum*) and *Ass. Trifolio-Agrimonetum* (Müll. 1961). Thicket communities were represented by *Ass. Salici-Franguletum* (Malc. 1929), whereas forest communities by – *Ass. Peucedano-Pinetum* (Mat. (1962) 1973). Two communities characteristic of cultivated-field communities were recorded on the eastern and northern side of the lake, behind the zone of meadow communities. Those were: *Ass. Vicietum tetraspermae* and *Ass. Galinsogo-Setarietum* (R. Tx. Et Beck. 1942) R. Tx. 1950) (Fig. 3) [14].

### Lake Zbyszewickie

In the littoral zone of the lake, *Ass. Nupharo-Nymphaetum albae* and also *Ass. Phragmitetum communis*, *Ass. Typhetum latifoliae* and *Ass. Scripetum lacustris* ((Allorge 1922) Chouard 1924) occurred. Meadow communities in the zone immediately surrounding the lake were represented by tall herb vegetation (*Ass. Filipendulo-Geraniatum*), *Ass. Sileno otitis-Festucetum*; (Libb. 1933), *Ass. Trifolio-Agrimonetum* and the grazing land from the order of *Arrhenatheretalia* (*Ass. Lolio-Cynosuretum*). On the western side, a patch of *Ass. Pruno-Crataegetum* (Hueck 1931) occurred, whereas on the eastern side – a patch of *Ass. Salici-Franguletum* and *Ass. Circaeo-Alnetum*. Behind the strip of meadow and thicket communities, the lands were covered with vegetation of field communities represented by *Ass. Vicietum tetraspermae* in the northern and southern part, and *Ass. Galinsogo-Setarietum* in the western and eastern part (Fig. 4) [14].

### Lake Pawłowski

*Ass. Nupharo-Nymphaetum albae*, as well as reed and bulrush communities (*Ass. Phragmitetum communis*, *Ass. Typhetum latifoliae*) were recorded in the littoral zone. Communities of reed beds were represented abundantly along the northern and southern side of the lake. Within the zone immediately around the lake, thicket communities occurred along the eastern and western side, represented by *Ass. Pruno-Crataegetum* and *Ass. Ligustro-Prunetum* (R. Tx. 1952), and also forest communities in the form of *Ass. Circaeo-Alnetum*. In the southern part, thicket communities turn into meadow communities represented by *Ass. Sileno otitis-Festucetum*, meadows from the order *Molinietalia* (*Ass. Cirsio-Polygonetum*), meadows from the order *Magnocaricetalia* (*Ass. Caricetum acutiformis*), grazing lands (*Ass. Lolio-Cynosuretum*) and the reed association (*Ass. Phragmitetum communis*). In the northern part, tall herb vegetation (*Ass. Filipendulo-Geraniatum*) occurred in the form of a small patch. Field communities occurred beyond the strip of thicket communities. Along the eastern side, they were represented by *Ass. Vicietum tetraspermae*, whereas along the western side – by *Ass. Vicietum tetraspermae*, *Ass. Papaveretum argemones* ((Libb. 1932) Krusem. et Vlieg. 1929) and *Ass. Galinsogo-Setarietum* (Fig. 5) [14].



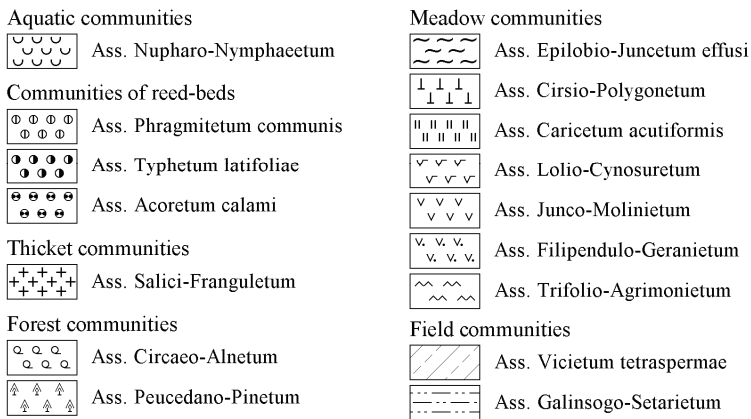
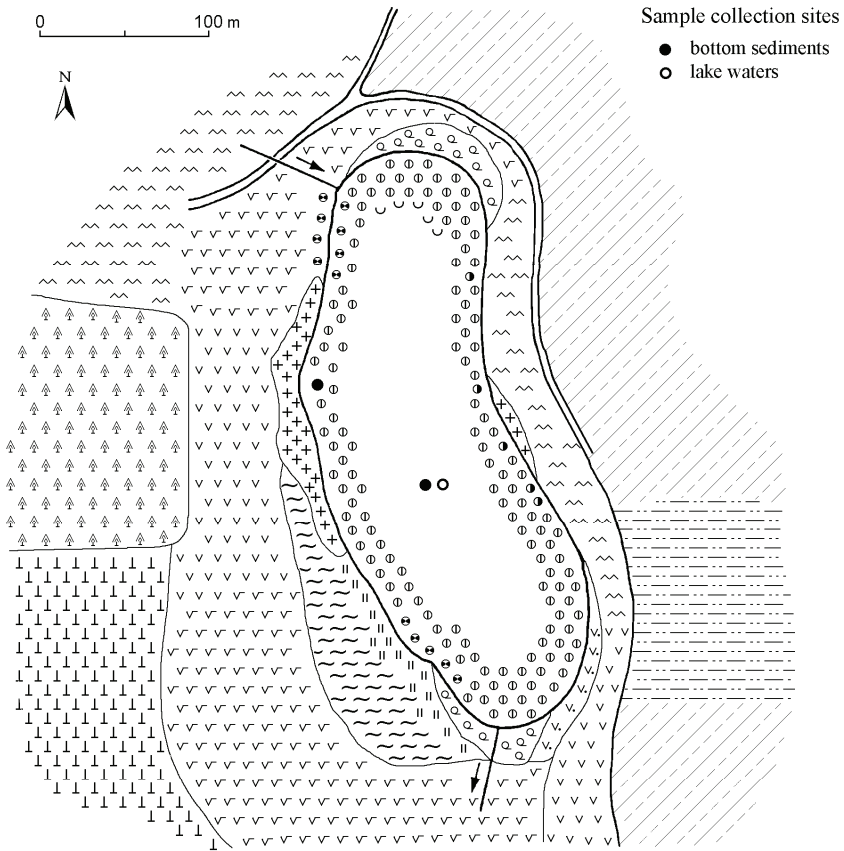


Fig. 3. Plant communities of the zone directly surrounding Lake Murwinek [14]

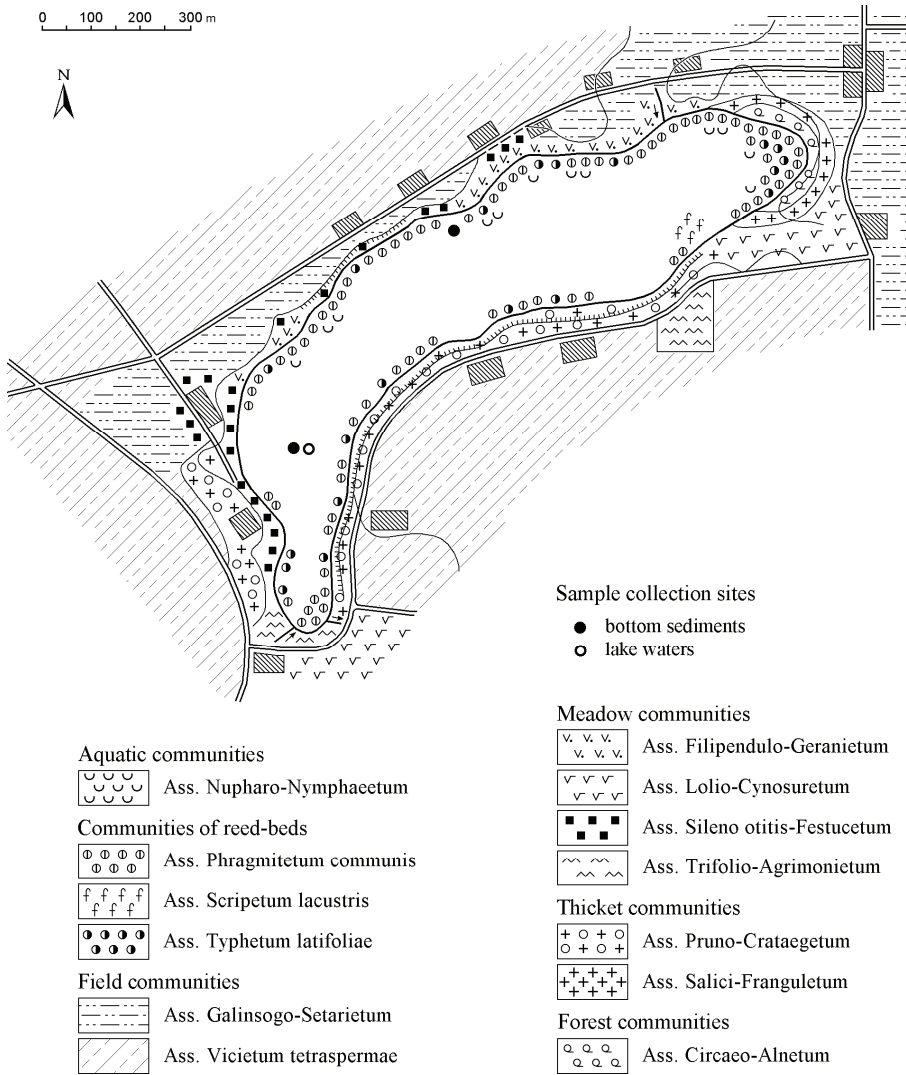


Fig. 4. Plant communities of the zone directly surrounding Lake Zbyszewickie [14]

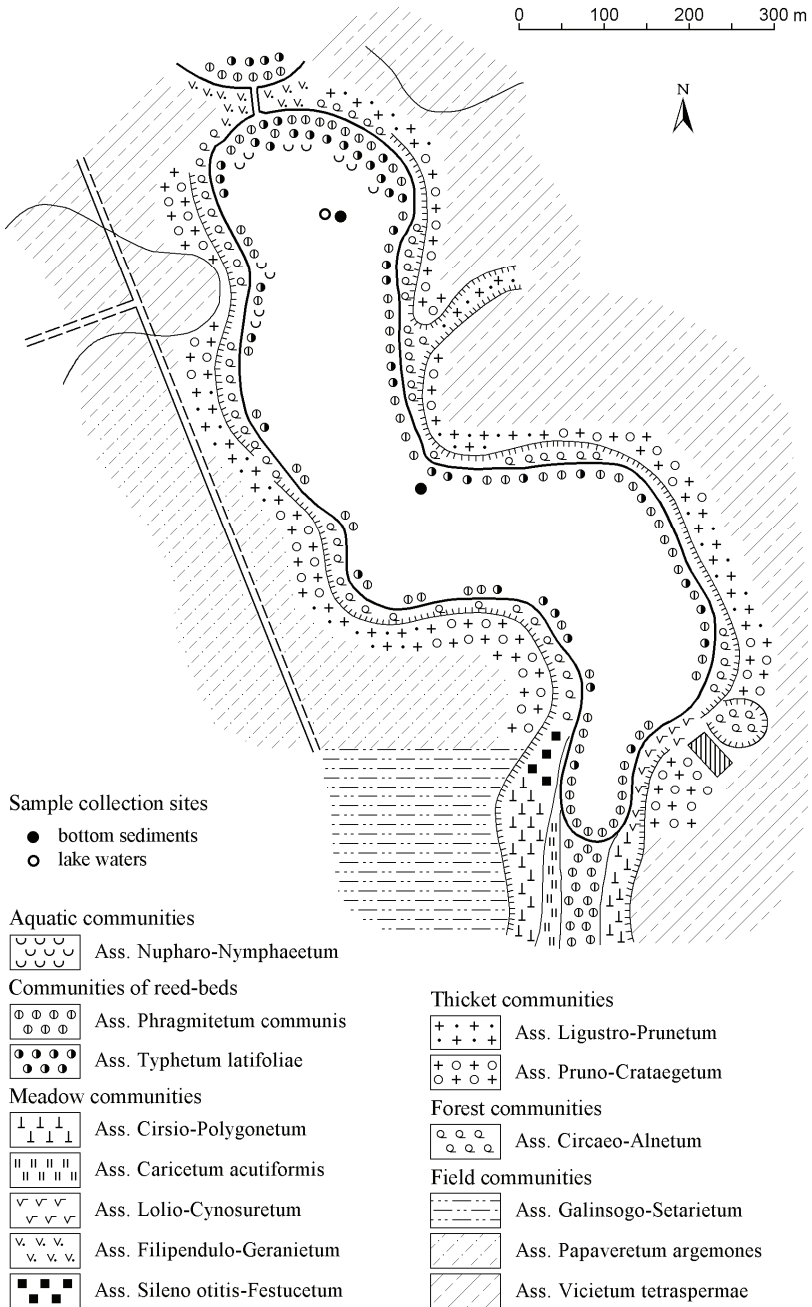


Fig. 5. Plant communities of the zone directly surrounding Lake Pawłowskie [14]

### Lake Czeszewskie

In the littoral zone, aquatic communities were represented by *Ass. Nupharo-Nymphaeetum albae*, whereas rush communities – by *Ass. Phragmitetum communis*, *Ass. Typhetum latifoliae* and *Ass. Scripetum lacustris*. Reed beds dominated and they were also present on the shore creating a large patch in the western part of the lake and a strip around the remaining part of the lake. Tall herb vegetation (*Ass. Filipendulo-Geraniatum*) occurred on the southern side of the lake in the form of small patches, whereas *Ass. Diantho-Armerietum* (Krausch 1959) forms a large patch. Meadows from the order of *Molinietalia* (*Ass. Cirsio-Polygonetum*) extended in the northern part of the lake, beyond the strip of rush vegetation. Within the rush vegetation, thickets of *Ass. Salici-Franguletum* occurred in the form of small patches and in the western part – patches of *Ass. Pruno-Crataegetum*. Further surroundings of the lake is covered by field communities represented by *Ass. Vicietum tetraspermae* and *Ass. Papaveretum argemones* (Fig. 6) [14].

### Lake Strzalkowo

*Ass. Nupharo-Nymphaeetum albae*, as well as reed and bulrush communities represented by *Ass. Phragmitetum communis* and *Ass. Typhetum latifoliae* were recorded in the littoral zone. A zone of meadow communities with small patches of communities representing thicket and forest communities extended around the lake. In the southern part of the lake, the occurrence of the meadow association from the order *Arrhenatheretalia* was recorded (*Ass. Arrhenatheretum medioeuropean* ((Br.-Bl. 1925) Koch 1926), and a small patch of *Ass. Salici-Franguletum* and *Ass. Circaeo-Alnetum*. In the northern part, patches of the following associations were recorded: meadows from the order *Molinietalia* (*Ass. Cirsio-Polygonetum*), grazing land from the order *Arrhenatheretalia* (*Ass. Lolio-Cynosuretum*) and tall herb vegetation (*Ass. Filipendulo-Geraniatum*). Behind them, communities of agricultural crops extended, represented by *Ass. Vicietum tetraspermae*. Whereas in the western part, within the zone adjacent to the lake, *Ass. Trifolio-Agrimonetum* and *Ass. Diantho-Armerietum* occurred. Behind this zone of meadow communities, field communities represented by *Ass. Galinsogo-Setarietum* occurred (Fig. 7) [14].

### Lake Żońskie

*Ass. Nupharo-Nymphaeetum albae*, as well as reed and bulrush communities (*Ass. Phragmitetum communis*, *Ass. Typhetum latifoliae*), were recorded in the littoral zone. Within the zone immediately around the lake, thicket communities *Ass. Salici-Franguletum*, *Ass. Pruno-Crataegetum* and *Ass. Ligustro-Prunetum* occurred along the eastern shoreline, as well as forest communities represented by *Ass. Circaeo-Alnetum* and *Ass. Peucedano-Pinetum*. In some places, tall herb vegetation (*Ass. Filipendulo-Geraniatum*) and *Ass. Papaveretum argemones* occurred. Behind the zone of thicket communities, *Ass. Vicietum tetraspermae* occurred, which represents the field communities. In the western part, patches of meadow communities occurred: *Ass. Caricetum elatae* (Koch 1926), *Ass. Epilobio-Juncetum effusi*, *Ass. Filipendulo-Geraniatum* and the forest community (*Ass. Circaeo-Alnetum*). Field communities were represented by *Ass. Vicietum tetraspermae* and *Ass. Papaveretum argemones* (Fig. 8) [14].

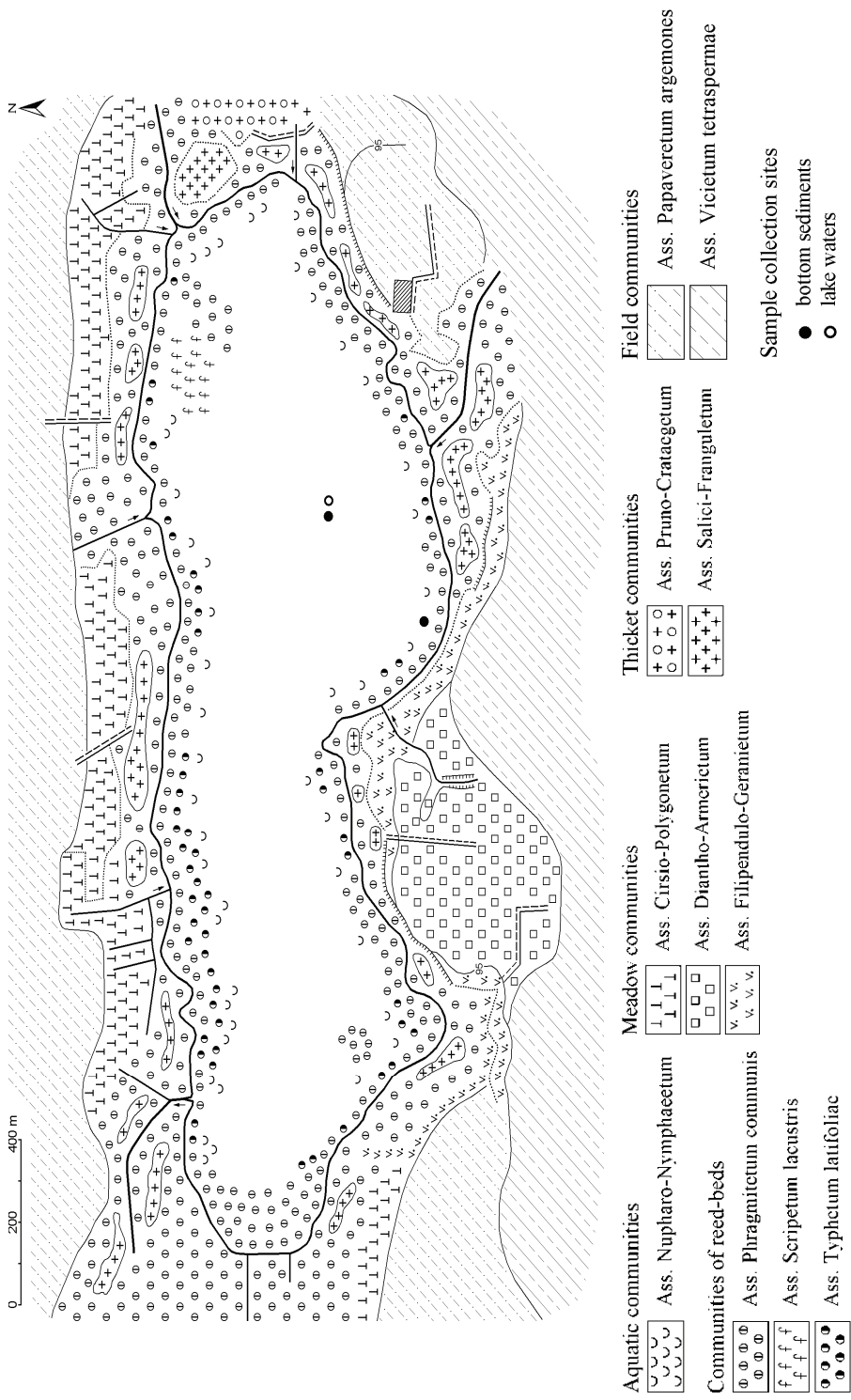


Fig. 6. Plant communities of the zone directly surrounding Lake Czeszewskie [14]

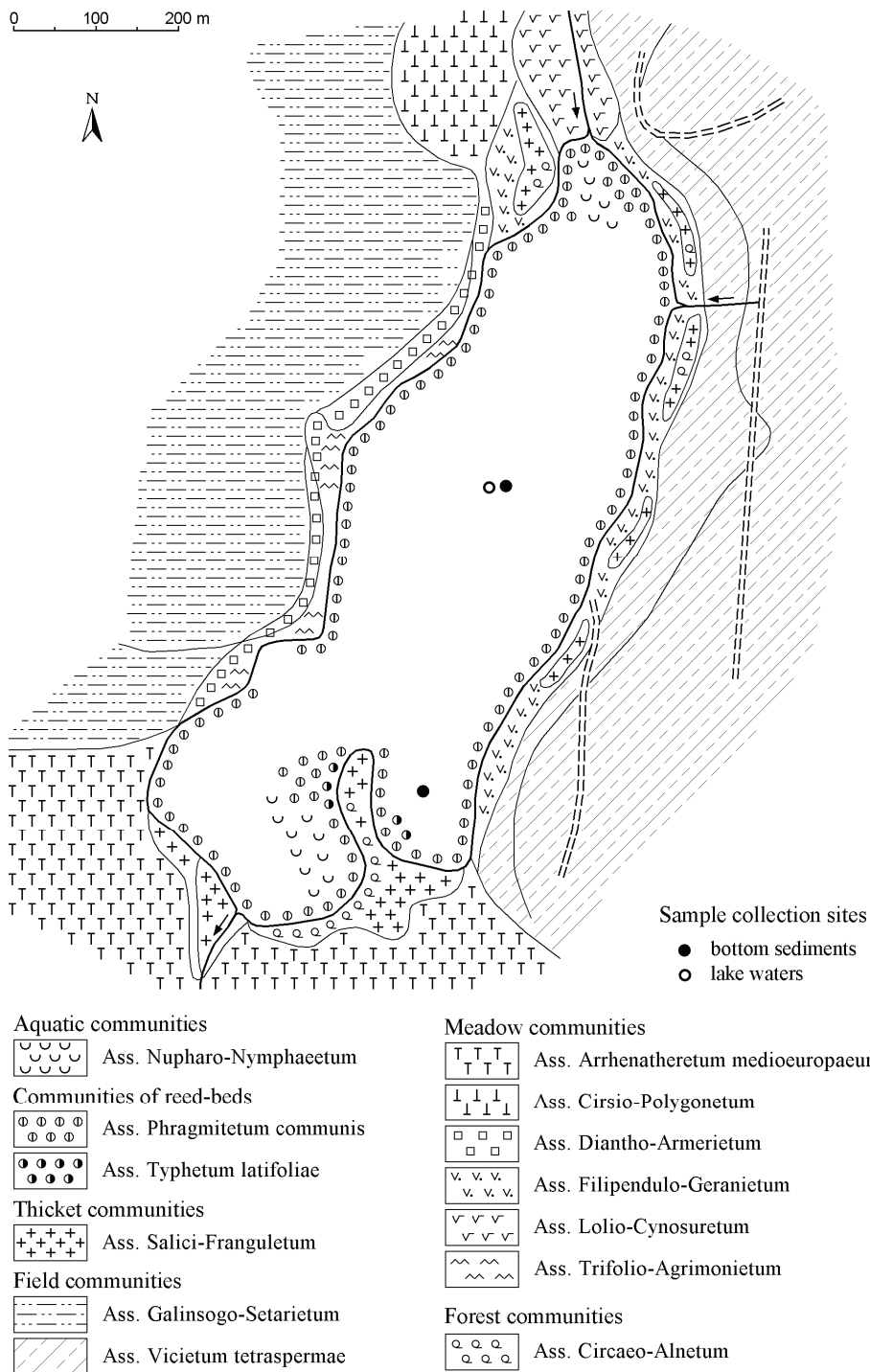
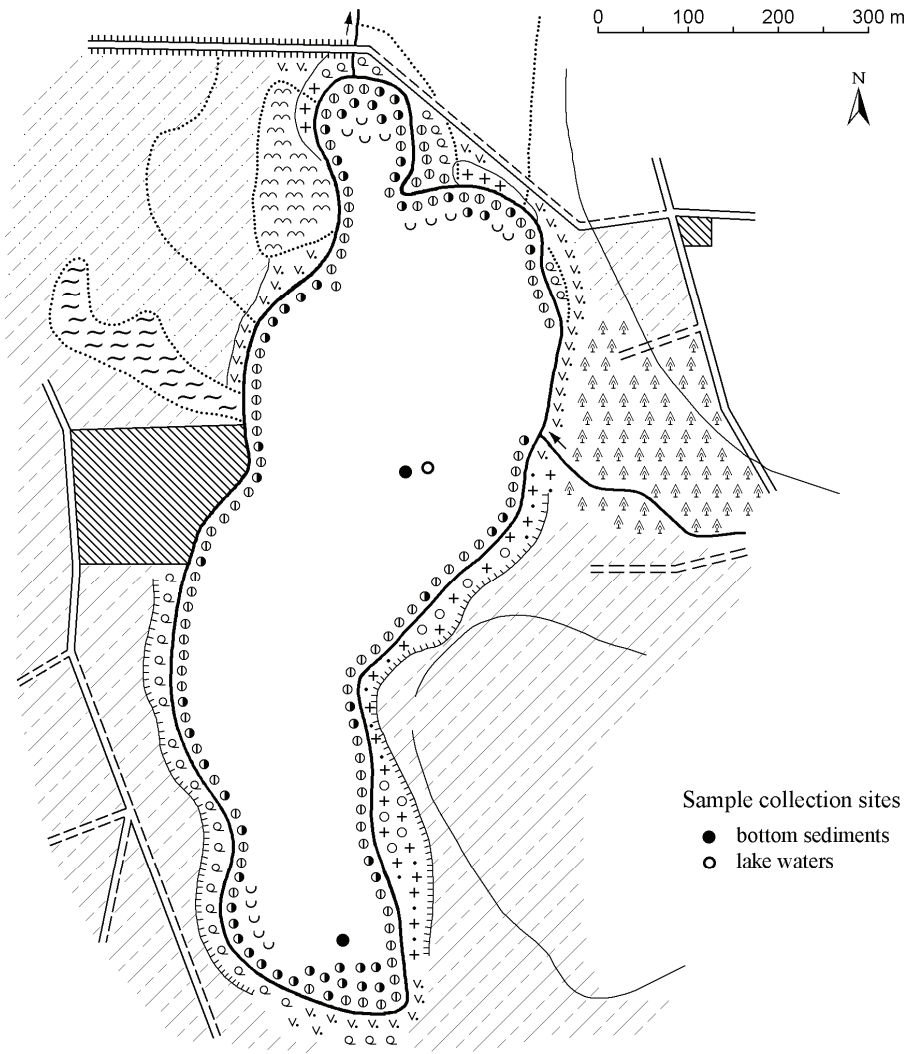



Fig. 7. Plant communities of the zone directly surrounding Lake Strzałkowo





Sample collection sites  
 ● bottom sediments  
 ○ lake waters

**Aquatic communities**


 Ass. Nupharo-Nymphaetum


**Communities of reed-beds**


 Ass. Phragmitetum communis

 Ass. Typhetum latifoliae


**Meadow communities**


 Ass. Caricetum elatae


 Ass. Epilobio-Juncetum effusi

 Ass. Filipendulo-Geranietum


**Thicket communities**


 Ass. Ligustro-Prunetum

 Ass. Pruno-Crataegetum


 Ass. Salici-Franguletum

**Forest communities**

 Ass. Circaeo-Alnetum

 Ass. Peucedano-Pinetum

**Field communities**

 Ass. Papaveretum argemones


 Ass. Vicietum tetraspermae

Fig. 8. Plant communities of the zone directly surrounding Lake Żońskie [14]

### Lake Czworokątne

Aquatic communities are represented by *Ass. Nupharo-Nymphaetum albae*, whereas reed beds by *Ass. Phragmitetum communis*. The zone immediately surrounding the lake includes thickets (*Ass. Salici-Franguletum*) situated in the north, which develop into *Ass. Circaeo-Alnetum*. Communities of grass and tall herbs are abundantly represented. Well developed *Ass. Galio silvatici-Carpinetum* and *Ass. Potentillo albae-Quercetum* (Libb. 1933) occur in the eastern and southern parts, patches of these associations occur also along the western side. In the vicinity of this lake, forest communities are also represented by *Ass. Quercu roboris-Pinetum* (J. Mat. (mscr.)). Along the western side of the lake, field plant communities represented by *Ass. Papaveretum argemones* were found (Fig. 9) [14].

### Lake Krąpsko Małe

The area adjacent to the lake was covered with *Ass. Circaeo-Alnetum* turning into *Ass. Ribo nigri-Alnetum* (Sol.-Górn. 1975 mscr.) in the north-western part, whereas in the south-eastern part – into meadow (*Ass. Caricetum acutiformis*). Also patches of *Ass. Stellario-Carpinetum* (Oberd. 1957) were found. Most of the area behind the strip of *Ass. Ribo nigri-Alnetum* (Sol.-Górn. 1975 mscr.) was covered with *Ass. Melico-Fagetum* (Lohm. Ap. Seibert 1954) turning into *Ass. Peucedano-Pinetum*. In the littoral zone, communities of aquatic plants included *Ass. Nupharo-Nymphaetum albae* and *Ass. Potamogetonetum perfoliati* (Koch 1926 em. Pass. 1964). Rush communities were represented by *Ass. Phragmitetum communis*, *Ass. Equisetum limonite* (Steffen 1931) and *Ass. Scripetum lacustris* (Fig. 10) [14].

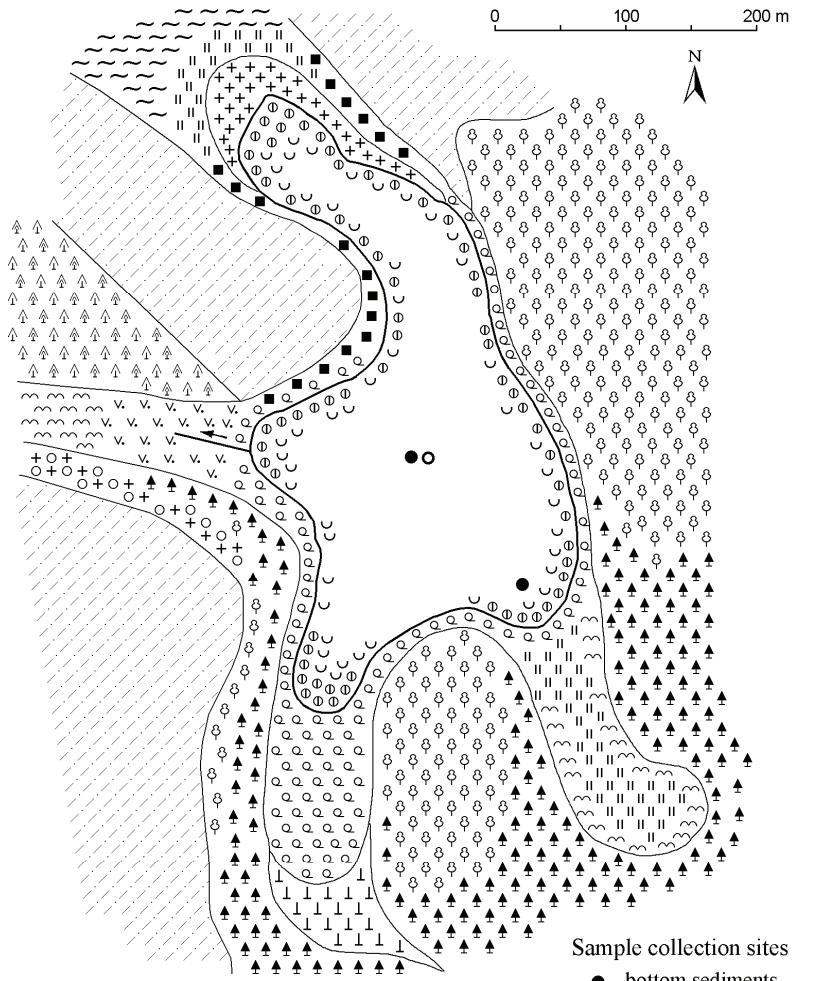
### Lake Sumile

Communities of aquatic plants were represented by *Ass. Nupharo-Nymphaetum albae* and *Ass. Potamogetonetum perfoliati*. Rush communities in the form of *Ass. Phragmitetum communis* and *Ass. Typhetum latifoliae* occurred in small quantities. In the zone adjacent to the lake, mainly *Ass. Circaeo-Alnetum* occurred, locally turning into *Ass. Ribo nigri-Alnetum*, *Ass. Tilio-Carpinetum* and meadow *Ass. Geranio-Peucedanetum cervariae*. Further on, these associations were turning into *Ass. Quercu roboris-Pinetum*. The island located on the lake was covered with grey-willow bushes and riparian mixed ash-alder forests in the vicinity of typical rush and aquatic communities (Fig. 11) [14].

### Lake Hanki

In the littoral zone, communities of aquatic plants were represented by *Ass. Nupharo-Nymphaetum albae* and rush communities in the form of *Ass. Phragmitetum communis* and *Ass. Typhetum latifoliae*. In the zone adjacent to the lake, *Ass. Circaeo-Alnetum* occurred together with small fragments of *Ass. Ribo nigri-Alnetum*. Patches of *Ass. Tilio-Carpinetum* occurred on the edges. Along the eastern side, alder woods were turning into a meadow from the order *Molinietalia* (*Ass. Epilobio-Juncetum effusi*), whereas along the south-western side – into *Ass. Sileno otitis-Festucetum*. Whereas in the north and in the west, *Ass. Quercu roboris-Pinetum* occurred. In the zone surrounding the lake, field communities were represented by *Ass. Aphano-Matricarietum* (R. Tx. 1937) corresponding to communities of fallow type (Fig. 12) [14].

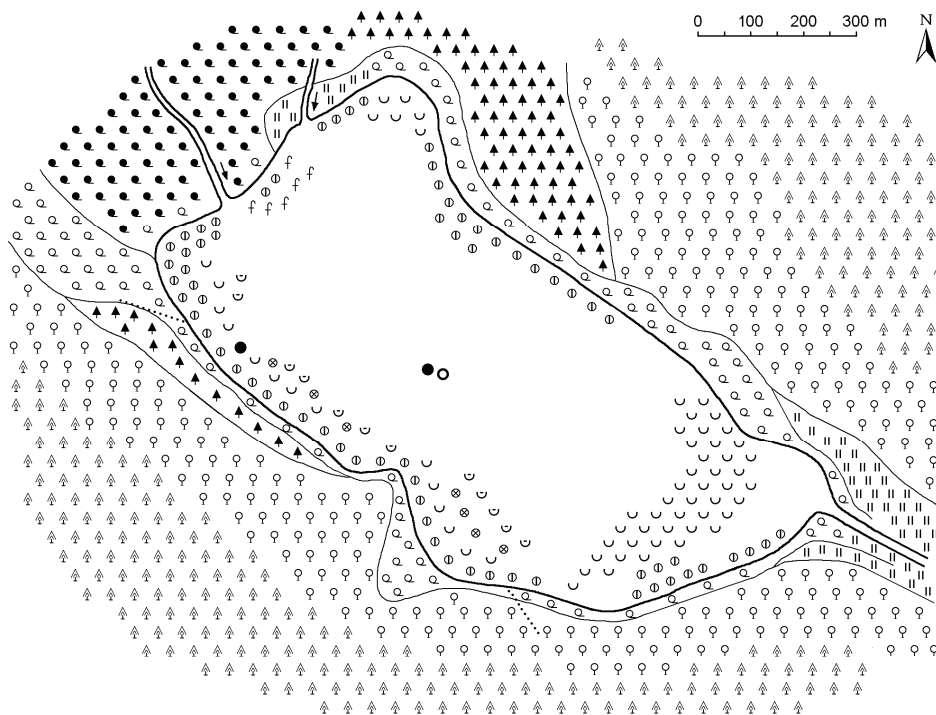




Sample collection sites  
 ● bottom sediments  
 ○ lake waters

- |                          |                               |                     |                                 |
|--------------------------|-------------------------------|---------------------|---------------------------------|
| Aquatic communities      |                               | Thicket communities |                                 |
|                          | Ass. Nupharo-Nymphaetum       |                     | Ass. Pruno-Crataegutum          |
| Communities of reed-beds |                               |                     | Ass. Salici-Franguletum         |
|                          | Ass. Phragmitetum communis    | Forest communities  |                                 |
| Meadow communities       |                               |                     | Ass. Circaeo-Alnetum            |
|                          | Ass. Caricetum acutiformis    |                     | Ass. Galio silvatici-Carpinetum |
|                          | Ass. Caricetum elatae         |                     | Ass. Potentillo albac-Quercetum |
|                          | Ass. Cirsio-Polygonetum       |                     | Ass. Querco roboris-Pinetum     |
|                          | Ass. Epilobio-Juncetum effusi | Field communities   |                                 |
|                          | Ass. Filipendulo-Geraniatum   |                     | Ass. Papaveretum argemones      |
|                          | Ass. Sileno otitis-Festucetum |                     |                                 |

Fig. 9. Plant communities of the zone directly surrounding Lake Czworokątne [14]



**Aquatic communities**

- Ass. Nupharo-Nymphaetum
- Ass. Potamogetonum perfoliati

**Communities of reed-beds**

- Ass. Phragmitetum communis
- Ass. Scirpetum lacustris
- Ass. Equisetum limosi

**Meadow communities**

- Ass. Caricetum acutiformis

**Forest communities**

- Ass. Ribo nigri-Alnetum
- Ass. Circaeo-Alnetum
- Ass. Stellario-Carpinetum
- Ass. Melico-Fagetum
- Ass. Peucedano-Pinetum

**Sample collection sites**

- bottom sediments
- lake waters

Fig. 10. Plant communities of the zone directly surrounding Lake Krapsko Male [14]

**Lake Borowe**

In the littoral zone, communities of aquatic plants were represented by *Ass. Nupharo-Nymphaetum albae* and rush communities in the form of *Ass. Phragmitetum communis* and *Ass. Typhetum latifoliae*. Reed beds were particularly well developed in the western part of the lake, where also a patch of bushes (*Ass. Salici-Franguletum*) was found. In the zone adjacent to the lake, on its western side, vegetation typical of a meadow from the order *Magnocaricetalia* occurred and was represented by *Ass. Caricetum elatae*, the remaining part of this zone was covered with *Ass. Circaeo-Alnetum*. Further surroundings of the lake were covered with *Ass. Quercu roboris-Pinetum*, turning into *Ass. Peucedano-Pinetum* (Fig. 13) [14].

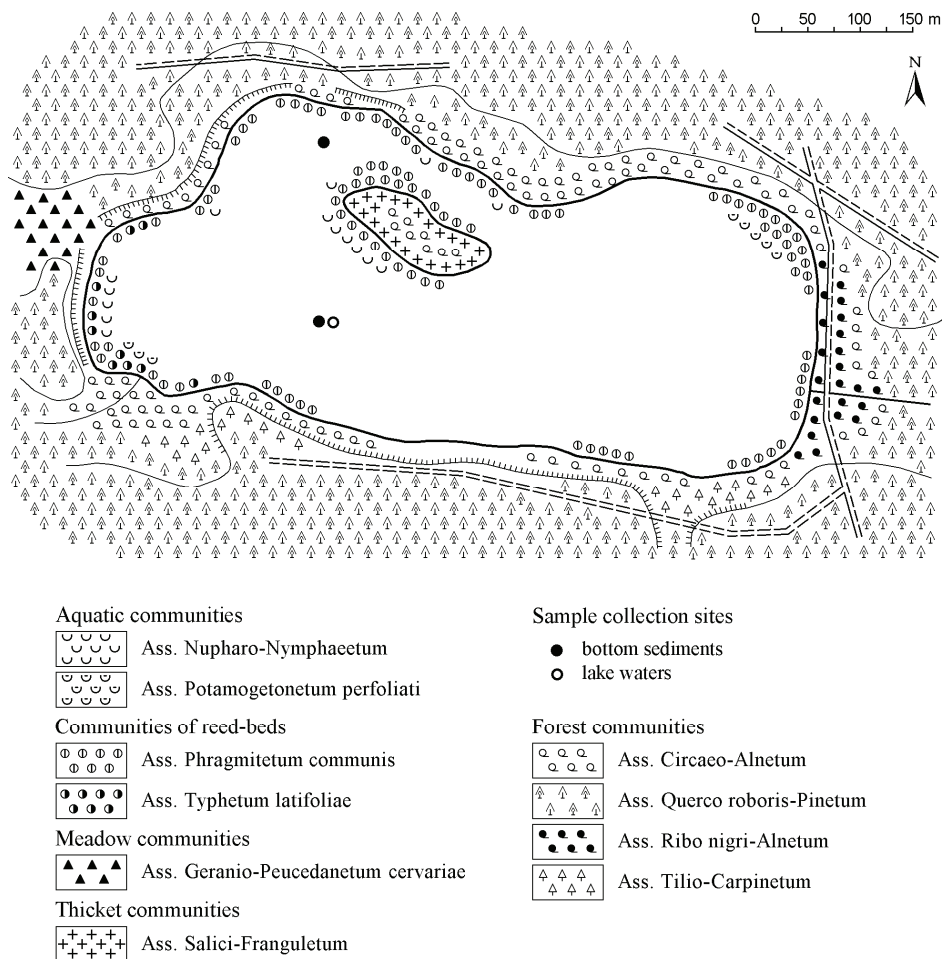


Fig. 11. Plant communities of the zone directly surrounding Lake Szamoty Duże [14]

### Lake Szamoty Duże

The littoral zone was characterized by the occurrence of numerous associations representing rush communities: *Ass. Phragmitetum communis*, *Ass. Typhetum latifoliae*, *Ass. Equisetum limosi*, *Ass. Acoetum calami*, *Ass. Scirpetum lacustris* and *Ass. Nupharo-Nymphaeetum albae* – a community of aquatic plants. In the immediate surroundings of the lake, on a steep slope in the north, meadow communities occurred, which included *Ass. Diantho-Armerietum* and *Ass. Sileno otitis-Festucetum*. In more humid places, tall herb vegetation was present (*Ass. Filipendulo-Geranietum*). In the north-eastern and southern part, bushes of *Ass. Salici-Franguletum* were found, and in the north-western part – of *Ass. Pruno-Crataegetum*. *Ass. Circaeo-Alnetum* occurred around the lake in the form of a rather narrow strip. In the eastern part, *Ass. Quercu roboris-Pinetum* was turning into *Ass. Potentillo albae-Quercetum*. Whereas, the western part was characterized by the occurrence of *Ass. Tilio-Carpinetum*. In this part, behind the zone of forest and thicket plant communities, field plant associations occurred: *Ass. Vicietum tetraspermae* and *Ass. Papaveretum argemones* (Fig. 14) [14].

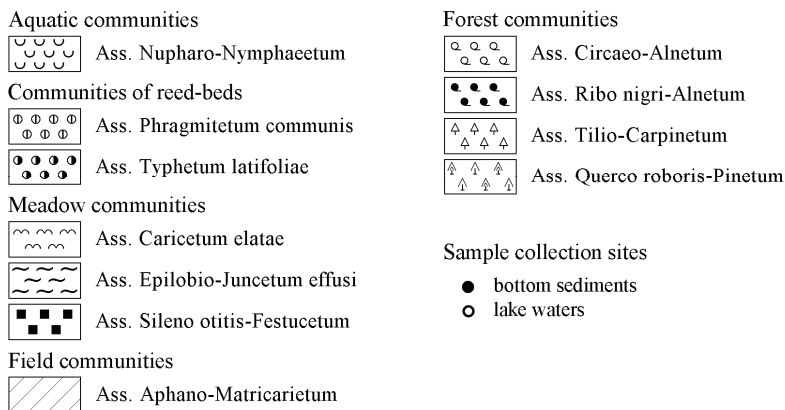
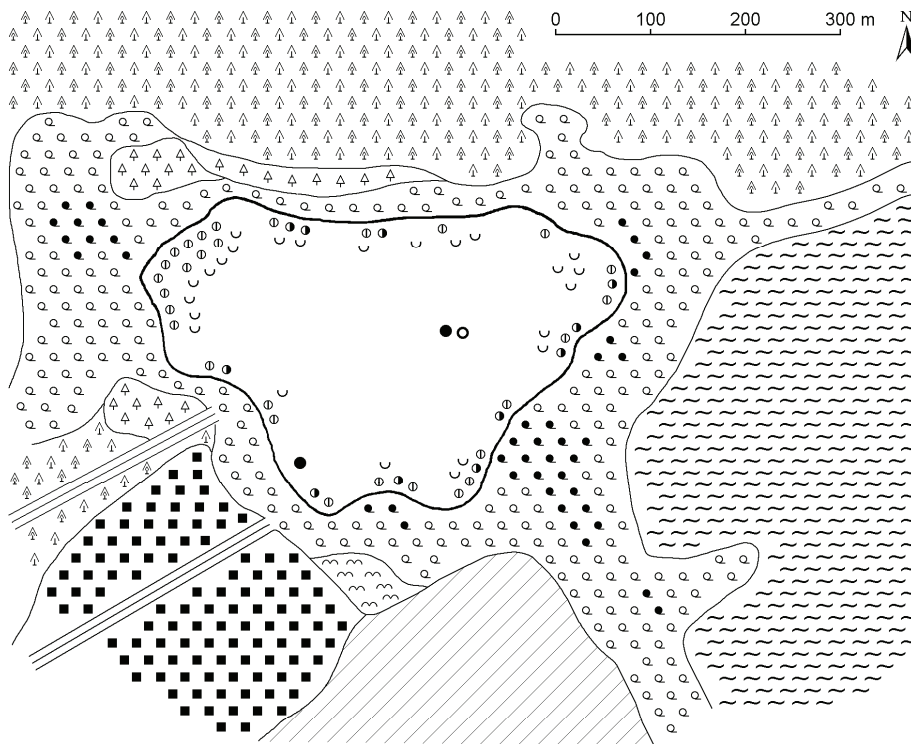


Fig. 12. Plant communities of the zone directly surrounding Lake Hanki [14]

### Lake Pniewo

Rush communities, which were represented by *Ass. Phragmitetum communis* and *Ass. Scripetum lacustris*, were particularly well developed in the eastern part of the lake. A small island on the lake was covered with reed beds. The area to the north and to the north-west of the lake was covered with *Ass. Quercu roboris-Pinetum*. The remaining part of the lake was surrounded by *Ass. Circaeo-Alnetum* turning into *Ass. Quercu roboris-Pinetum* and *Ass. Potentillo albae-Quercetum*. Thicket communities were

represented by *Ass. Salici-Franguletum*, which in the form of a larger patch occurred in the north-eastern part of the zone surrounding the lake. In the southern part, behind the zone of forest plant communities, field communities occurred, represented by *Ass. Vicietum tetraspermae* (Fig. 15) [14].

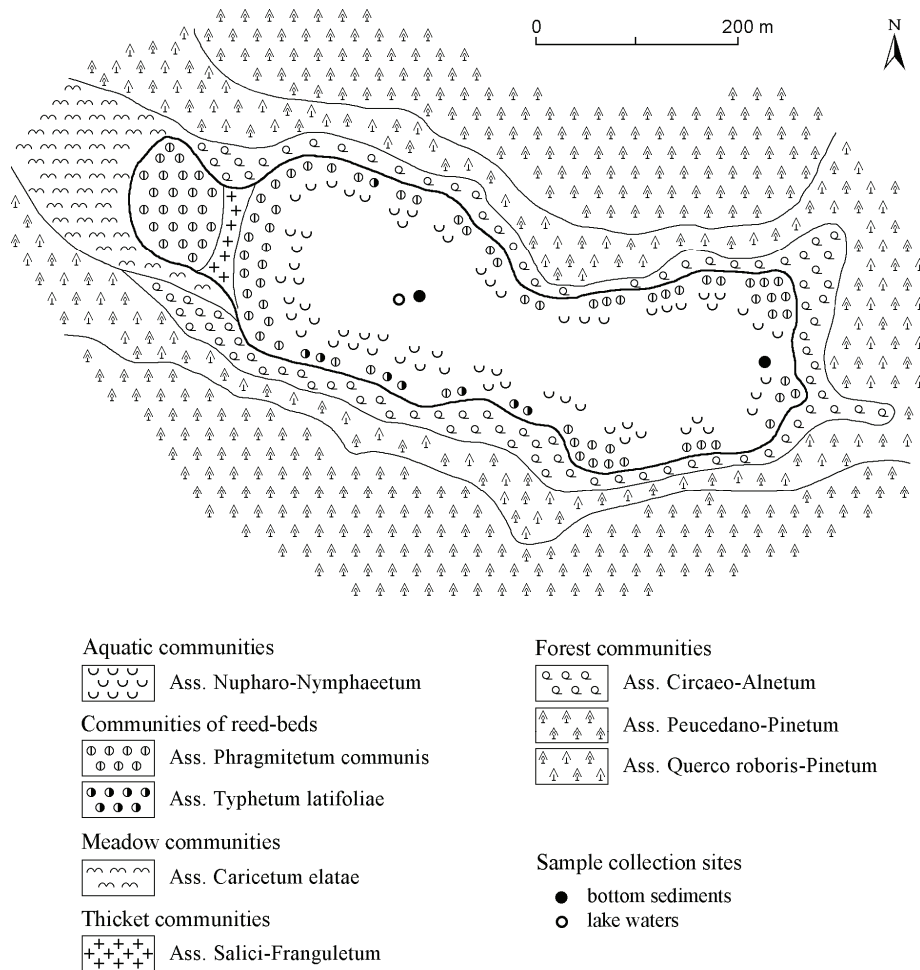


Fig. 13. Plant communities of the zone directly surrounding Lake Borowe [14]

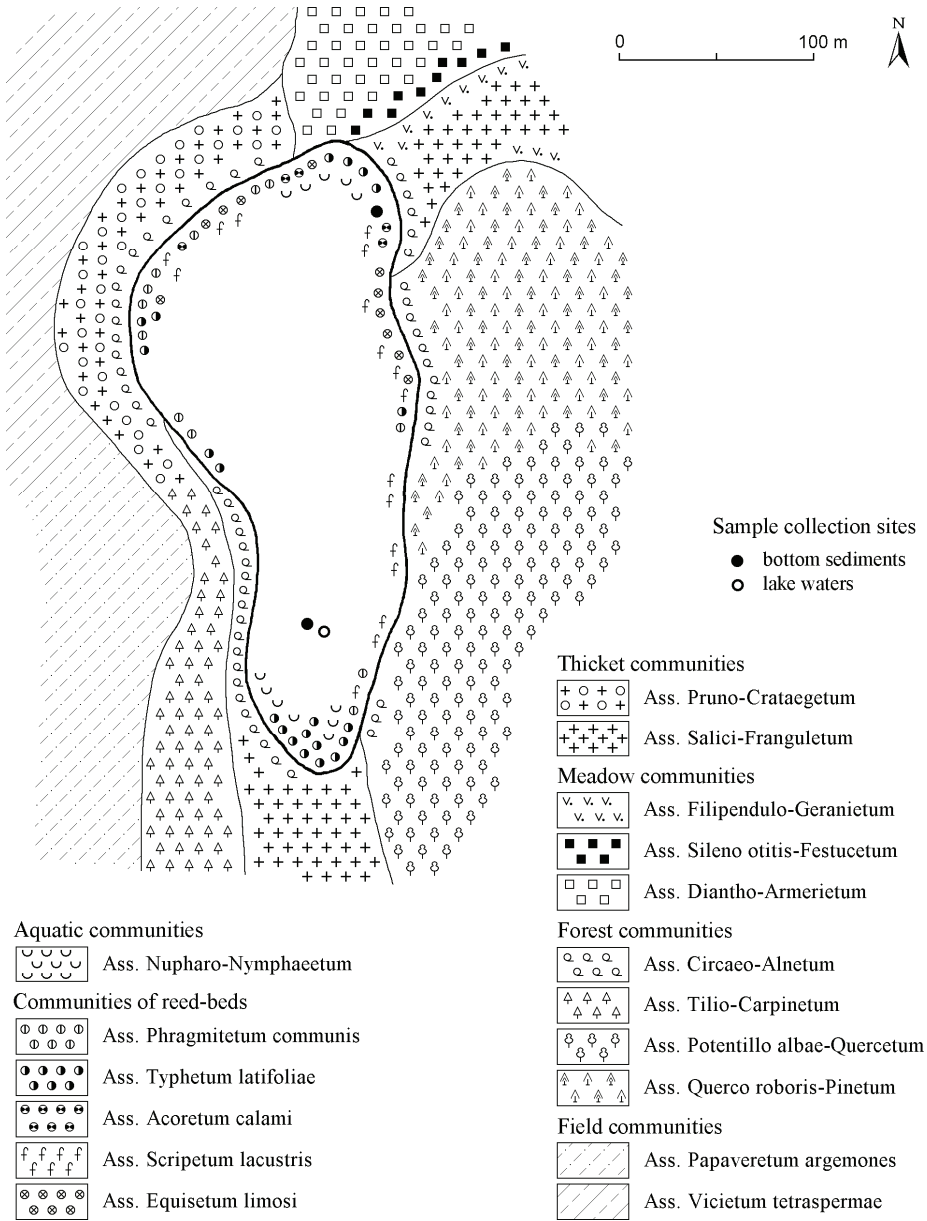


Fig. 14. Plant communities of the zone directly surrounding Lake Szamoty Duże [14]

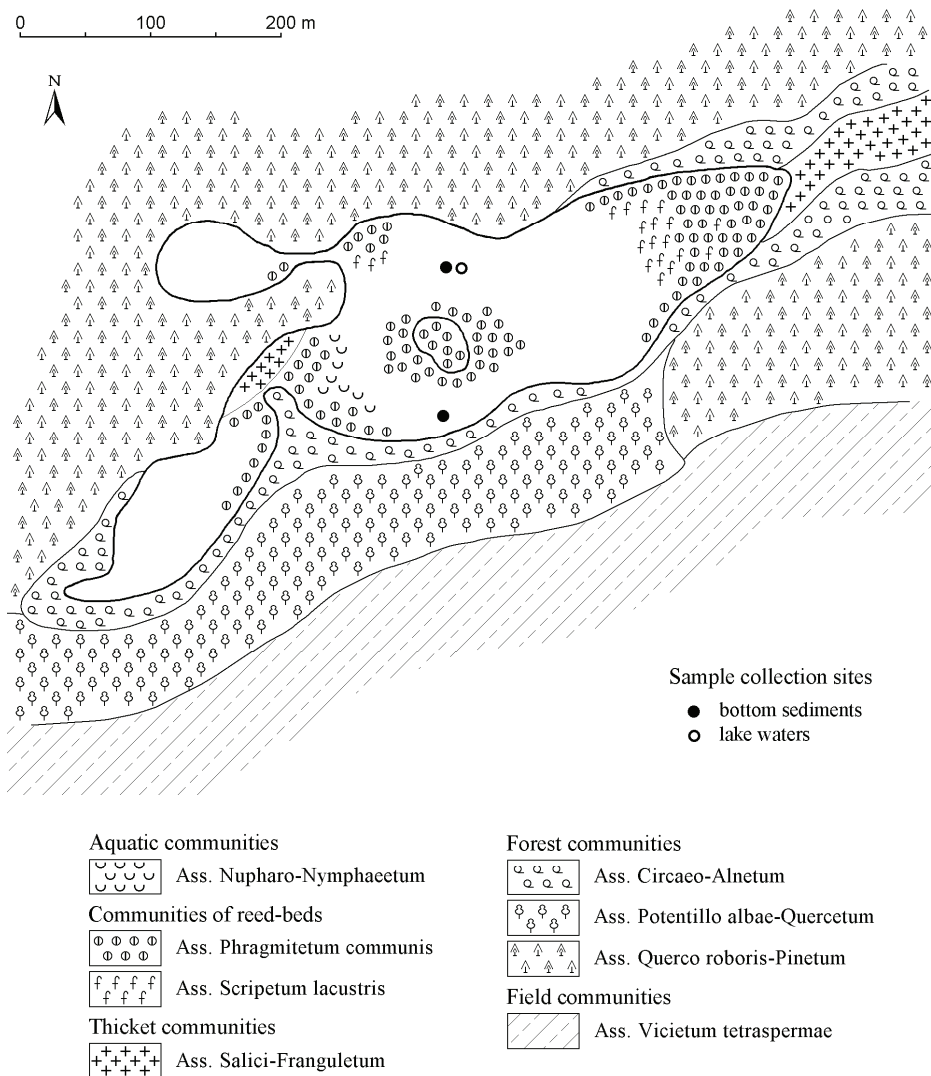


Fig. 15. Plant communities of the zone directly surrounding Lake Pniewo [14]

## 2.4. LAKE WATER

### 2.4.1. Physicochemical properties of the lake water

The composition of natural water is influenced by the geological structure of catchment area, climate, the type of soil and vegetation cover.

**Mineral carbon compounds** in inland waters occur in the form of the sustainable system of carbon dioxide, as well as bicarbonate and carbonate ions ( $\text{CO}_2\text{--HCO}_3^- \text{--CO}_3^{2-}$ ). The system is a major source of carbon in the photosynthesis of aquatic plants, and also all changes in the reaction of aquatic environment follow through this system. A decrease in the content of carbon dioxide, e.g. due to uptake during photosynthesis, causes alkalization of the environment due to the fact that the saturated solution of

calcium carbonate is produced. This carbonate can precipitate from the solution. It settles on the bottom or just covers the plants, it can also become a component material of lacustrine chalk. This process is defined as biological decalcification of water. Pondweed (*Potamogeton*), waterweed (*Elodea*) and other macrophytes have the ability to precipitate carbonate. With intensive photosynthesis, plants can use carbon dioxide from carbonate ions, which results in the appearance of hydroxyl ions. This may also occur as a result of dehydration of bicarbonate ions. With the inhibition of photosynthesis and the inflow of CO<sub>2</sub>, the cycle of transformations is reversed. Calcium bicarbonate as a salt of a weak acid also acts as a buffer and prevents bigger changes in the water reaction. In the presence of strong acids or their salts and bases, they are neutralized. These reactions do not cause the release of ions H<sup>+</sup> and OH<sup>-</sup> [65, 80].

**Chlorides** occur in different quantities in natural water. They can come from the soil, from natural salt beds and from contamination reaching the surface water. Chlorides from natural sources, the quantity of which is constant for a given territory and an aquifer, are called “normal”. Strong deviation indicates contamination or inflow from other aquifers.

The natural water contains chlorides in the quantity from some traces to several hundred mg·dm<sup>-3</sup>. Salty taste of water, caused by chlorides, is variable and is determined by the composition of water. Some waters containing 250 mg·dm<sup>-3</sup>, can have detectable salty taste if chlorides occur together with sodium ion. When calcium and magnesium ions dominate, there is no salty taste even with the concentration of 1000 mg·dm<sup>-3</sup> [35].

**Sulphur** in inorganic compounds occurs in the form of SO<sub>4</sub><sup>2-</sup> anion and as hydrogen sulphide (H<sub>2</sub>S). Sulphur gets into the surface water in the form of sulphates from the atmosphere together with rain or it is washed out from the substrate, whereas hydrogen sulphide is released during the decomposition of proteins. In anaerobic conditions, hydrogen sulphide constitutes a source of energy for sulphur bacteria, which reduce sulphates to hydrogen sulphide. Other colourless sulphur bacteria, e.g. *Beggiatoa*, are able to oxidate hydrogen sulphide. Transformations of sulphur forms are most intensive in bottom sediments [65].

**Phosphorus** is thought to be a chemical element that regulates the biological productivity in a reservoir, because it is essential to living organisms as an energy carrier and it occurs in such small quantities that its deficiency may quickly prove to be decisive. The ability of phosphorus to create various compounds is complicated by the simultaneous occurrence of calcium and iron in the water, and also it is determined by the water reaction. In the environment with neutral or slightly alkaline reaction, the phosphate ion is bound to calcium, in the alkaline environment – to sodium, whereas in water with acid reaction – to iron ions [13, 65]. Phosphorus is deposited not only in the form bound to dead organic matter, but also bound to iron, calcium, aluminium ions and mineral suspension. Basically, the higher the content of Fe, Ca, Al and suspended matter, the faster the precipitation of phosphorus from the water column. This process is also determined by the water reaction, e.g. the minimum solubility of FePO<sub>4</sub> is at pH = 5.5. The processes of sorption and release of phosphorus compounds from bottom sediments have a strong influence on the content of phosphorus in the water. Phosphates are quickly accumulated by bottom sediments and slowly move back into the water column. Polyphosphates occurring in sediments are slowly transformed into phosphates. Processes of phosphorus exchange between water and bottom sediments are largely determined by oxygen conditions, temperature (they are faster at higher temperatures),



reaction (they are faster at low pH), the redox potential and the surface of bottom sediments. It was also observed that in anaerobic conditions the return of phosphates to the water column is three times faster compared with aerobic conditions [20].

Resuspension is a very important factor influencing the release of phosphates from the bottom sediments. It is generally assumed that during resuspension there is greater potential to release phosphates from the sediment due to the increased contact area between sediment particles and lake water. Wiśniewski [91] concluded, based on the researches conducted in the Włocławek Reservoir, that both adsorption and desorption of phosphates can take place in the pelagic zone during sediment resuspension. Direction of the process depends mainly on the concentration of phosphates in the bottom water. In the described reservoir, the release of phosphates into the pelagic zone occurs only when the bottom water contains up to ca. 0,3 mg of phosphates  $\cdot \text{dm}^{-3}$ . In the case of higher concentrations, irrespective of oxygen conditions, phosphates are absorbed proportionally to their concentration in the bottom water.

Based on the obtained results, it was found that the direction of the process depends on the following factors (listed below in the order of importance):

- the gradient of phosphates' concentrations within the contact zone between water and bottom sediments,
- the content of oxygen in the bottom water during resuspension,
- the granulometric composition of sediments, and more precisely – the contribution of fine particles, remaining in the suspension for a long time [91].

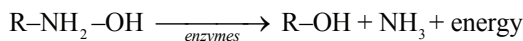
In the aquatic environment **iron** reacts with the bicarbonate anion and phosphoric acid anion. In slightly acid or neutral waters, and in the presence of oxygen, iron(II) is oxidized to iron(III). Iron(III) salts are hydrolyzed and insoluble hydroxide ( $\text{Fe}(\text{OH})_3$ ) is precipitated. This way ferruginous sediment is precipitated, which in time can create beds of meadow ore. The occurrence of iron compounds in the water is also very important due to their large redox potential. Iron in the form of dissolved mineral compounds can stay in neutral and acid waters devoid of oxygen. This happens in the hypolimnion of eu- and dystrophic lakes. In different conditions, iron is precipitated and accumulated as sediment. On this basis, it can be concluded that in the epilimnion there are no conditions to maintain iron in the solution; if detected then only in a small quantity in the colloidal state. Whereas in the hypolimnion of eutrophic lakes, there are complete conditions for transition of  $\text{Fe}^{3+}$  into the solution. This can lead to a certain concentration of soluble iron in deep layers of hypolimnion. The process of dissolution and precipitation of iron compounds is inversely proportional to oxygenation and distribution of oxygen in a water reservoir. In the conditions of alkaline reaction, the presence of hydrogen sulphide can cause precipitation of iron sulphide. Due to the capability of creating compounds with phosphate ions of different solubility, iron is involved in the iron-phosphate cycle [20, 65].

**Nitrogen compounds** play an important role in the processes occurring in natural waters. Huge amounts of nitrogen occur in the atmosphere in the form of gas (on average 78%).  $\text{NO}_x$  are produced during electric discharges in the atmosphere, and together with water they build nitric (V) acid. This acid reaches the surface of the Earth together with precipitation. Also the production of nitrogenous fertilizers is important to the nitrogen balance. The thus obtained nitrogen compounds are used on cultivated fields as a fertilizer, from where some of them get into rivers and water reservoirs.

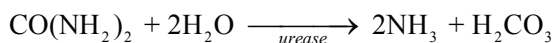
Free nitrogen dissolved in water is absorbed by some algae and bacteria. Nitrogen fixation by aquatic organisms is an important source of nitrogen in the water. Nitrate

and ammonium salts occurring in the water are absorbed by plants as a necessary component in the process of biosynthesis (assimilation).

Animal organisms are not capable of using the nitrogen from the atmosphere or producing the proteins from inorganic compounds. Therefore they uptake the protein from other plants and animals. After plants and animals die, their residues are decomposed in the biochemical process, and then nitrogen from organic compounds turns into ammonia nitrogen. This process of protein mineralization is called ammonification or desamination. Although the process is very complex, it can be presented in a simplified way:



Part of the nitrogen is excreted by animals in faeces and urine. The nitrogen occurs there in the form of urea, which is quickly oxidized in the water to ammonia:



Part of the released ammonia in aerobic conditions is oxidized to nitrates(III) and then to nitrates(V) in the presence of bacteria (*Nitrosomonas*, *Nitrobacter*). In anaerobic conditions,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  are reduced to nitrogen oxides or free nitrogen. Denitrifying bacteria (*Achromobacter agile*, *Chromobacter denitrificans*, *Pseudomonas denitrificans*, *Bacillus denitrificans*) are involved in this process. Denitrification occurs in the benthic zone of water reservoirs, where there are anaerobic zones, and in the bottom sediments. Bottom sediments play a significant role in the circulation of nitrogen in a water reservoir. After settling on the bottom of a reservoir, plant and animal remains are mineralized, and partially they are the food for benthic fauna, which in turn is consumed by fish. In the presence of oxygen, the processes of nitrification may occur.

The concentrations of organic nitrogen in the surface waters may change within the range from decimals to a few  $\text{mg N}\cdot\text{dm}^{-3}$ . In the case of serious water contamination, they can reach several  $\text{mg N}\cdot\text{dm}^{-3}$ .

In the surface water, the concentrations of ammonia nitrogen range from the hundredth parts to a few  $\text{mg N}\cdot\text{dm}^{-3}$ . The presence of ammonia nitrogen in the water results from several factors, including the following most important ones: the inflow of ammonia from point and nonpoint sources, the development of aquatic vegetation, aerobic conditions and temperature. The content of ammonia nitrogen is characterized by considerable fluctuations during the year. Concentrations of ammonia are very small during seasons with higher temperatures when ammonia is used by plants and when is included in the process of nitrification. Whereas in winter, during seasons with low temperatures, when biological life disappears in water and the process of nitrification is inhibited, the concentration of ammonium ions increases.

Nitrates(III) are transitional compounds in the biological cycle. They are created in the process of biochemical oxidation of ammonia. They are relatively instable and they are quickly transformed into nitrates(V) in the aerobic environment in the presence of microorganisms.

Nitrates(V) are substances necessary for life of aquatic plants (including phytoplankton). Therefore the concentration of nitrates(V) in water bodies is often determined by the development of biomass. During growing seasons, the concentrations of nitrates(V) decrease to very small values, and then increase again in winter [20].

**Magnesium** in the form of compounds usually occurs in the surface and underground water. Their content in the water depends on geological conditions of aquifers and drainage area of a river. The concentration of magnesium compounds is generally lower than the concentration of calcium compounds (the average ratio 1:4). Similarly to calcium compounds, magnesium compounds cause water hardness [35].

**Calcium** is the main cation in most surface waters. The concentration of calcium in water can range from a few to several hundred  $\text{mg}\cdot\text{dm}^{-3}$ , and to a large extent depends on the carbonate equilibrium. Calcium can be precipitated or transferred from deposits into water depending on the prevailing physicochemical conditions. High content of calcium in the surface water results from intensive outwashing of rocks from the soil. In our climate, calcium (and also magnesium) is intensively washed out from agricultural lands. Eluviation contributes to acidification of precipitation, and consequently also the soil [20].

**Electrical conductivity** of water depends on the content of dissolved ionic components. Due to a small degree of dissociation, both clean water and water contaminated with organic components hardly conduct electric current. Using the determined electrical conductivity, one can indirectly calculate the content of dry residue or salinity. Differences in electrical conductivity between lakes result from the structure of water supply to a lake, and at the same time from the individual nature of a given catchment area. Also seasonal changes in conductivity are encountered. Most often higher values occur in spring, and between spring and summer they usually do not exceed  $50 \mu\text{S}\cdot\text{cm}^{-1}$ . The biggest seasonal changes are observed in the most shallow lakes. In the case of lakes with the developed thermal stratification, higher conductivity occurs in bottom layers, whereas differences between surface and bottom water do not exceed  $50 \mu\text{S}\cdot\text{cm}^{-1}$  [20].

The range of **pH** for lentic water fluctuates between 6.5 and 8.5. In most cases, waters of lakes are slightly alkaline or neutral. Water flowing from wetlands and forests are usually acid due to the presence of humic and fulvic acids. Precipitation has a significant influence on acidification of surface waters [20].

Water **transparency** is determined by the occurrence of suspended matter, the presence of which impedes the penetration of light and consequently limits a water photosynthetic layer in deep water bodies. Turbidity of water, particularly when it is caused by mud or clay particles, often acts as a limiting factor. Whereas, in the situations when it is caused by the presence of living organisms, measurements of water transparency become an indicator of water productivity. Transparency determined by the Secchi disk fluctuates between a few cm and 40 m in very transparent but not particularly productive lakes [20].

#### 2.4.2. Trophic types of lakes

Depending on the age of a lake and its individual characteristics (morphometric type, nature of the surrounding area, water exchange rate, characteristics of a catchment area), a reservoir evolves and the final stage of this evolution process is disappearance of a lake, which is brought about by the fact that a lake basin becomes more and more shallow due to deposition of organic and mineral materials, and due to increased run-off. During the process of evolution, more and more nutrients reach a lake. It is believed that the main factor inducing the increased trophic status of a lake is the content of phosphorus compounds, sometimes also the content of nitrogen, and exceptionally carbon.

The most universal are trophic typologies, which divide lakes according to their productivity, therefore initially only oligotrophic and eutrophic lakes were distinguished. Thienemann [84] extended this division to the third type – dystrophic lakes. Furthermore, he extended the aforementioned classification to the following groups:

- 1) lakes with a harmonious development, characterized by little variation of factors that determine the development of organisms. This group includes:
  - oligotrophic lakes, when the amount of dissolved oxygen does not drop below 20%, and phosphates and nitrates occur in small quantities,
  - eutrophic lakes, when the amount of dissolved oxygen is lower than 20%, whereas phosphates and nitrates occur in medium and large quantities,
- 2) unilaterally developed lakes, which are characterized by the excess of one of the environmental factors:
  - dystrophic lakes where the excess of humus substances colours the water dark brown,
  - alkalitrophic lakes, which contain the excess of calcium,
  - argilitrophic lakes where the cycle of matter is affected by argillaceous particles,
  - acidotrophic lakes characterized by considerable acidification,
  - siderotrophic lakes in which iron compounds play an important role.

At present, the above group should include saprotrophic lakes, i.e. contaminated with waste waters. Stangenberg's division [78], modified by Wiszniewski [90] is an example of applying the typology of Thienemann to Polish lakes (Fig. 16).

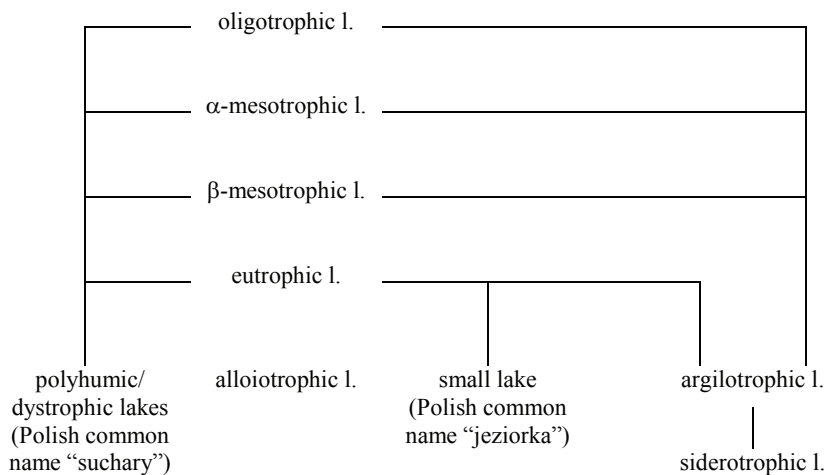


Fig. 16. Diagram presenting the evolution of lakes according to Stangenberg [78] modified by Wiszniewski [90]

The researches indicate that if the evolution is harmonious from oligotrophy to eutrophy, it does not always proceed according to this scheme. Extremely oligotrophic Tatra lakes are one of the examples – in the process of evolution they directly turn into dystrophy.

In the light of processes and phenomena, in which humic acids dissolved in water are involved, as well as based on paleolimnological data, the situation of lakes rich in these substances looks slightly different. A different scheme of lakes' evolution in

Poland was presented by Górnjak [31]. It assumes the possibility that dystrophic lakes can function as a transitional stage before an eutrophic stage (small lake) (Fig. 17).

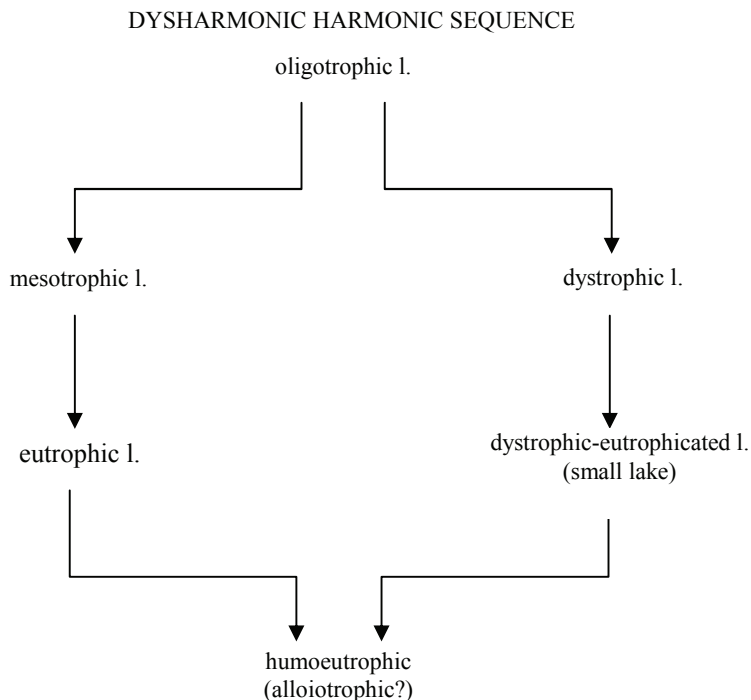


Fig. 17. Diagram of lakes' evolution in Poland [31]

The development of lakes can be much more complex, and considerable, seasonal water fluctuations can additionally enhance this. For lakes with a considerable high depth, this does not matter much, but several-metre changes in the water level in the case of lakes with small average depths have tremendous influence on the evolution of the trophic type. The rising water level induces the process of detrophication, whereas during subsequent changes of water levels, the trophic status can increase or decrease. This kind of phenomenon is defined by Gołębiewski [27] as reversion (recurrence) of trophism.

Studies on the trophic development of lakes allowed us to refine the previously distinguished types. At present, one can distinguish the following types of waters [28, 98]:

- **ultraoligotrophic waters** – extremely infertile waters characterized by exceptionally small production of phytoplankton, just a few grams of carbon bound under  $1 \text{ m}^2$  of surface water ( $\text{g C} \cdot \text{m}^{-2}$ ) per year. Waters of these lakes are very rich in oxygen, and this is expressed by almost complete mineralization of sediments. The bottom of these lakes is often similar to original (primary) rock. The littoral zone is almost completely devoid of macrophytes,

- **oligotrophic waters** are infertile, poor in nutrients. Annual production of phytoplankton is small, ca.  $10\text{-}30 \text{ g C} \cdot \text{m}^{-2}$ . Oxygenation of waters in the summer

exceeds 60%, and at the same time mineralization of deposits intensifies; they contain ca. 10% of organic matter; the littoral vegetation is scanty,

- **$\alpha$ -mesotrophic waters** are poor in nutrients, average annual production of plankton comes to 30-60 g C·m<sup>-2</sup>. Oxygenation of these waters in the abyssal zones ranges from 20 to 60% saturation. Together with inconsiderable oxygenation, the amount of organic matter increases to 20%. Dark mud similar to sapropel predominates at the bottom. Shoreline vegetation is quite well-developed,

- **$\beta$ -mesotrophic waters** are relatively fertile and rich in nutrients. Production of phytoplankton per year comes to 60-120 g C·m<sup>-2</sup>. In general, oxygenation of benthic waters does not exceed 30% of saturation. Bottom sediments of these water reservoirs contain ca. 25% of organic matter. Shoreline vegetation is well developed,

- **eutrophic waters** are fertile waters with high abundance of nutrients. Annual production of phytoplankton ranges from 120 to 200 g C·m<sup>-2</sup>. The zone of shoreline vegetation is well developed, and often covers a considerable part of a lake. In the summer, oxygenation of abyssal waters does not exceed 20% of saturation, and often drops to zero. Mineralization of sediments is inconsiderable and the contribution of organic matter ranges from 30 to as much as 60%. Eutrophic lakes are usually shallow, the bottom is covered by sediments with several metre thickness, where intensive saprogenic processes occur,

- **polytrophic waters** are characterized by exceptionally high annual production of phytoplankton – 200-400 g C·m<sup>-2</sup>. Sometimes the zone of littoral vegetation is not particularly well developed. Polytrophic reservoirs are very shallow and their maximum depths do not exceed 5 m. Due to this fact, waters of the benthic zone can be highly oxygenated. Owing to considerable production of organic matter, bottom sediments are low mineralized,

- **hypertrophic waters** are over-eutrophicated, usually with disturbed biological production, which varies within a broad range. Due to excessive loads of organic matter, bottom sediments occur in the form of a poorly decomposed sludge with the intense smell of hydrogen sulphide.

### 2.4.3. Water quality classes

The classification of surface waters is governed by the Regulation of the Ministry of Environment. Pursuant to the regulation of 2004, five-degree classification of inland surface waters was introduced (Journal of Laws/ of 2004 No. 32, item 284 [73]). Amendment to the regulation of 2008 (Journal of Laws/ of 2008 No. 162, item 1008 [74]) left the 5-degree classification, only parameters included in the assessment were changed (Tables 4 and 5). Whereas the system of quality assessment and classification of lakes proposed by Kudelska and the co-author [49] (Table 6) includes the evaluation of susceptibility of lakes to degradation and the lake water quality assessment. The term of water quality (purity) classes should be based on the total assessment of all water quality indices, and the determination of a lake's category – on all indices describing the susceptibility of a reservoir to degradation. Table 4 presents the indices and their standard values for 3 classes of lake water quality. The following scoring was adopted for particular classes: class I – 1 point, class II – 2 points, class III – 3 points and outside the class – 4 points. Based on the obtained results, the arithmetic mean is calculated and referred to the presented limits: class I  $\leq 1.50$  points, class II  $\leq 2.50$  points, class III  $\leq 3.25$  points and  $> 3.25$  points outside the class. The accepted set of indices is used for the general ecological assessment of the lake water quality.

Table 4. Limit values of the water quality indices related to homogeneous surface waters, such as a lake or another natural water body [74]

Number of the water quality index	Name of the water quality index	The limit value of the water quality index, appropriate for class					Remarks	
		unit	I	II	III	IV		V
1	2	3	4	5	6	7	8	9
Biological elements								
1.1	Phytoplankton							
	Chlorophyll "a"							
1.1.1	Schindler's coefficient < 2 <sup>1)</sup>	µg l <sup>-1</sup>	< 5	8	11	16	> 16	average value <sup>2)</sup>
	Schindler's coefficient > 2 <sup>1)</sup>	µg l <sup>-1</sup>	< 7	13	21	33	> 33	average value <sup>2)</sup>
	Schindler's coefficient < 2 <sup>3)</sup>	µg l <sup>-1</sup>	< 10	19	30	42	> 42	average value <sup>2)</sup>
	Schindler's coefficient > 2 <sup>3)</sup>	µg l <sup>-1</sup>	< 10	23	40	68	> 68	average value <sup>2)</sup>
1.2	Phytobenthos							
1.2.1	Diatom Index for lakes OI <sup>4)</sup>	-	> 0.83	0.55	0.30	0.15	< 0.15	
1.3	Macrophytes							
1.3.1	Ecological State Macrophyte Index <sup>5)</sup>	-	1-0.680	0.679-0.340	0.339-0.170	0.169-0.090	< 0.090	
	Ecological State Macrophyte Index <sup>6)</sup>	-	1-0.680	0.679-0.270	0.269-0.110	0.109-0.050	< 0.050	
1.4	Benthic macroinvertebrates	The element not included in the classification of waters (reference conditions in the process of determination)						
1.5	Ichthyofauna	The element not included in the classification of waters (reference conditions in the process of determination)						
2	Hydromorphological elements (supporting a biological element)							
2.1	Hydrological regime							
2.1.1.a	Volume and the dynamics of the water flow, the level	Until the numerical limit values are determined, one should assume that a limit value of class I is as follows: the size and the dynamics of the flow, the level, the retention time and the resulting connections with the subterranean waters, corresponding to completely undisturbed or similar conditions. Typically, the limit values for other classes are not determined						
2.1.2	Connection with subterranean waters							
2.1.3	Retention time							
2.3	Morphological conditions							
2.3.1.b	Variation in the depth							
2.3.2.b	Quantitative structure and the substrate of the bottom	Until the numerical limit values are determined, one should assume that a limit value of class II is as follows: variation in the depth of the homogeneous waters, the amount and the structure of the substrate, as well as the structure and the state of the shoreline zone corresponding to completely undisturbed or similar conditions. Typically, the limit values for other classes are not determined						
2.3.3.b	Shore structure of a lake and other natural or artificial water reservoirs							



Table 4 continued

1	2	3	4	5	6	7	8	9
3	Physicochemical elements (supporting a biological element)							
3.1	A group of indices describing the physical state, including thermal conditions							
	Transparency – Secchi disk visibility							
3.1.4	Schindler's coefficient < 2 <sup>1)</sup> Schindler's coefficient > 2 <sup>1)</sup> Schindler's coefficient < 2 <sup>3)</sup> Schindler's coefficient > 2 <sup>3)</sup>	m m m m	2.5 1.7 1.5 1				Typically, limit values are not determined	average value <sup>2)</sup> average value <sup>2)</sup> average value <sup>2)</sup> average value <sup>2)</sup>
3.2	A group of indices describing aerobic conditions (oxygenation conditions) and organic contaminants							
3.2.1	Dissolved oxygen <sup>7)</sup>	mgO <sub>2</sub> l <sup>-1</sup>		≥ 4			Typically, limit values are not determined	
3.2.5	Average oxygen saturation of hypolimnion	%		≥ 10				
3.3	A group of indices characterizing the salinity							
3.3.2	Conductivity in 20°C	μS·cm <sup>-1</sup>		≤ 600 <sup>8)</sup>			Typically, limit values are not determined	
3.5	A group of indices describing biogenic conditions (biogenic substances)							
	Total nitrogen							
3.5.5	Schindler's coefficient < 2 <sup>1)</sup> Schindler's coefficient > 2 <sup>1)</sup> Schindler's coefficient < 2 <sup>3)</sup> Schindler's coefficient > 2 <sup>3)</sup>	mg N l <sup>-1</sup> mg N l <sup>-1</sup> mg N l <sup>-1</sup> mg N l <sup>-1</sup>	1.5 2 1.6 2.5				Typically, limit values are not determined	average value <sup>3)</sup> average value <sup>2)</sup> average value <sup>2)</sup> average value <sup>2)</sup>
	Total phosphorus							
3.5.7	Schindler's coefficient < 2 <sup>1)</sup> Schindler's coefficient > 2 <sup>1)</sup> Schindler's coefficient < 2 <sup>3)</sup> Schindler's coefficient > 2 <sup>3)</sup>	mg P l <sup>-1</sup> mg P l <sup>-1</sup> mg P l <sup>-1</sup> mg P l <sup>-1</sup>	0.060 0.090 0.100 0.120				Typically, limit values are not determined	average value <sup>3)</sup> average value <sup>2)</sup> average value <sup>2)</sup> average value <sup>2)</sup>

Explanatory notes:

- 1) for stratified lakes
- 2) the arithmetic average from the research results obtained at one measuring location
- 3) for unstratified lakes
- 4) for all lakes, except for lakes being under the influence of seawaters and unstratified lakes with Schindler's coefficient < 2 and the Ca content > 25 mg l<sup>-1</sup>
- 5) for deep Chara lakes
- 6) for shallow Chara lakes
- 7) summer, the near-bottom layer

Table 5. Limit values of the water quality indices from the group of substances particularly harmful to aquatic environment (specific synthetic and non-synthetic contaminants) corresponding to good and more than good ecological conditions of homogeneous surface waters [74]

CAS <sup>1)</sup> number for chemical substances	The water quality index number	The name of the water quality index	Unit	Limit values of the water quality indices according to categories of homogeneous surface waters		
				stream, rivulet, brook, river (including strongly transformed ones), channel	lakes, strongly transformed lakes, and other natural and artificial water reservoirs	internal seawaters, transitional and coastal waters
1	2	3	4	5	6	
	4	A group of chemical indices characterizing the occurrence of substances particularly harmful to aquatic environment				
	4.3.	Specific synthetic and non-synthetic contaminants (concentrations of metals refer to the dissolved phase)				
7440-38-2	4.3.1	Arsenic	mg As·l <sup>-1</sup>	0.05	0.05	
7440-39-3	4.3.2	Barium	mg Ba·l <sup>-1</sup>	0.5	0.5	
7440-42-8	4.3.3	Boron	mg B·l <sup>-1</sup>	2	2	
none	4.3.4	Hexavalent chromium	mg Cr <sup>+6</sup> ·l <sup>-1</sup>	0.02	0.02	
7440-47-3	4.3.5	Total chromium (total of Cr <sup>3+</sup> and Cr <sup>+6</sup> )	mg Cr·l <sup>-1</sup>	0.05	0.05	
7440-66-6	4.3.6	Zinc	mg Zn·l <sup>-1</sup>	1	1	
7440-50-8	4.3.7	Copper	mg Cu·l <sup>-1</sup>	0.05	0.05	
none	4.3.8	Volatile phenols (the phenol index)	mg·l <sup>-1</sup>	0.01	0.01	
none	4.3.9	Petroleum hydrocarbons – the oil index	mg·l <sup>-1</sup>	0.2	0.2	
7429-90-5	4.3.10	Aluminium	mg Al·l <sup>-1</sup>	0.4	0.4	
57-12-5	4.3.11	Free cyanides	mg CN·l <sup>-1</sup>	0.05	0.05	
none	4.3.12	Bound cyanides	mg Me(CN) <sub>x</sub> ·l <sup>-1</sup>	0.05	0.05	
7439-98-7	4.3.13	Molybdenum	mg Mo·l <sup>-1</sup>	0.04	0.04	
7782-49-2	4.3.14	Selenium	mg Se·l <sup>-1</sup>	0.02	0.02	
7440-22-4	4.3.15	Silver	mg Ag·l <sup>-1</sup>	0.005	0.005	
15035-09-3	4.3.16	Thallium	mg Tl·l <sup>-1</sup>	0.002	0.002	
7440-32-6	4.3.17	Titanium	mg Ti·l <sup>-1</sup>	0.05	0.05	

Table 5 continued

1	2	3	4	5	6
14867-38-0	4.3.18	Vanadium	mg V·l <sup>-1</sup>	0.05	0.05
35734-21-5	4.3.19	Antimony	mg Sb·l <sup>-1</sup>	0.002	0.002
none	4.3.20	Fluorides	mg F·l <sup>-1</sup>	1.5	1.5
1932-52-9	4.3.21	Beryllium	mg Be·l <sup>-1</sup>	0.0008	0.0008
7440-48-4	4.3.22	Cobalt	mg Co·l <sup>-1</sup>	0.05	0.05
none	4.3.23	Tin <sup>2)</sup>	mg Sn·l <sup>-1</sup>	—	—

Explanatory notes:

- <sup>1)</sup> the number assigned to a substance by the American organization Chemical Abstracts Service (CAS)
- <sup>2)</sup> the index not included in the classification of waters (reference conditions in the process of determination)

Table 6. Indices and their standard values for 3 classes of lake water quality [49]

Index	Sampling time and location	Lake-water quality class		
		I	II	III
Average oxygen saturation of hypolimnion (s.l.)	summer	≥ 40	≥ 20	≥ 5
Dissoved oxygen (ns.l.)	summer, the near-bottom layer	≥ 4	≥ 2	≥ 1
COD by the dichromate method (s.l. + ns.l.)	summer, the surface layer	≤ 20	≤ 30	≤ 50
BOD <sub>5</sub> (s.l. + ns.l.)	summer, the surface layer	≤ 2	≤ 4	≤ 8
BOD <sub>5</sub> (s.l.)	summer, the near-bottom layer	≤ 2	≤ 5	≤ 10
Phosphates (s.l. + ns.l.)	spring, the surface layer	≤ 0.02	≤ 0.04	≤ 0.08
Phosphates (s.l.)	summer, the near-bottom layer	≤ 0.02	≤ 0.04	≤ 0.08
Total phosphorus (s.l.)	summer, the near-bottom layer	≤ 0.06	≤ 0.15	≤ 0.60
Total phosphorus (s.l. + ns.l.)	spring and summer (the average value), the surface layer	≤ 0.05	≤ 0.10	≤ 0.20
Mineral nitrogen (N <sub>NH4</sub> +N <sub>NO2</sub> ) (s.l. + ns.l.)	spring, the surface layer	≤ 0.2	≤ 0.4	≤ 0.8
Ammonia nitrogen (s.l.)	summer, the near-bottom layer	≤ 0.2	≤ 1.0	≤ 5.0
Total nitrogen (s.l.+ ns.l.)	spring and summer (the average value), the surface layer	≤ 1.0	≤ 1.5	≤ 2.0
Electrical conductivity (s.l.+ ns.l.)	spring, the surface layer	≤ 250	≤ 300	≤ 350
Chlorophyll a (s.l. + ns.l.)	spring and summer (the average value), the surface layer	≤ 8	≤ 15	≤ 25
Dry matter of seston (s.l. + ns.l.)	spring and summer (the average value), the surface layer	≤ 4	≤ 8	≤ 12
Secchi disk visibility (s.l. + ns.l.)	spring and summer (the average value)	≥ 4	≥ 2	≥ 1
Faecal coli titre (s.l. + ns.l.)	spring and summer, below the surface and above the bottom (the worst result)	≥ 1	≥ 0.1	≥ 0.01
Biological field observations (s.l. + ns.l.)	the whole year, the entire lake	the occurrence of fish kills or large-scale mortality of other aquatic organisms (both in the littoral and pelagic zones) exclude a lake from a quality class regardless of the value of other indices		

s.l. – stratified lakes, ns.l. – non-stratified lakes

#### 2.4.4. Characteristics of water

Water samples for the analyses were collected during spring circulation from the surface layer (1 m below the surface), and during summer stagnation from the surface layer and the bottom layer (1 m above the bottom) within the area of the maximum depth (the deepest place of a lake basin). In the case of Lake Murwinek, due to a small depth of this reservoir, samples were collected from 1/2 of the maximum depth. The transparency of lake waters was determined with the Secchi disk. Water samples for the determination of nitrogen with Kjeldahl's method and ammonia nitrogen were fixed with the concentrated sulphuric(VI) acid [35].

The following parameters were determined in the analysed samples:

- pH by the electrometric method,
- specific conductivity by the conductometric method,
- the total content of iron by the colorimetric method with o-phenanthroline,
- the content of calcium by the complexometric method with disodium versenate in relation to calces,
- the content of magnesium by the complexometric method with disodium versenate in relation to eriochrome black T,
- the content of ammonia nitrogen by the colorimetric method with Nessler's reagent,
- the content of nitrate nitrogen(V) by the colorimetric method with  $\alpha$ -naphthylamine,
- the total content of organic and ammonia nitrogen by Kjeldahl's method (in the case of waters, the total content of nitrogen means the total content of nitrate nitrogen(V) and nitrogen determined with Kjeldahl's method),
- the content of orthophosphates (V) by the colorimetric method with ammonium heptamolybdate(VI) in relation to tin(II) chloride,
- the content of chlorides by the spectrophotometric method with silver nitrate(V) and potassium chromate(VI),
- the content of sulphates(VI) by the nephelometric method with barium chloride,
- the content of bicarbonates by the titrimetric method 0.005 M H<sub>2</sub>SO<sub>4</sub> in relation to methyl orange and phenolphthalein.

Waters **of field lakes** during *spring circulation* were characterized by a slightly alkaline and alkaline reaction, pH of these waters ranged from 7.85 (Lake Czeszewskie) to 8.79 (Lake Bobrów). The content of dissolved mineral compounds influenced the specific conductivity of water. Electrical conductivity varied – the highest value of 1257  $\mu\text{S}\cdot\text{cm}^{-1}$  was recorded for waters of Lake Czeszewskie, and the lowest one for waters of Lake Bobrów – 323  $\mu\text{S}\cdot\text{cm}^{-1}$ . The water transparency was 0.4-1.5 m. Total iron occurred in the concentrations from 0.08 to 0.25  $\text{mg}\cdot\text{dm}^{-3}$ . Most waters of the field lakes were rich in calcium and magnesium ions. The content of calcium was within the range of 43.1-200.4  $\text{mg}\cdot\text{dm}^{-3}$ , whereas the content of magnesium – within the range of 10.3-25.5  $\text{mg}\cdot\text{dm}^{-3}$ . The lowest content of calcium and magnesium was recorded for waters of Lake Bobrów, whereas the highest concentrations of ions Ca<sup>2+</sup> and Mg<sup>2+</sup> were recorded in waters of Lake Czeszewskie. Ammonia nitrogen occurred in waters of these lakes in small concentrations, and its content ranged from 0.01 (Lake Zbyszewickie) to 0.62  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Strzałkowo). The content of nitrate nitrogen(V) was higher compared with ammonia nitrogen and ranged from 0.723 (Lake Czeszewskie) to 2.15  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Żońskie). The content of orthophosphates(V) ranged from 0.05 (Lake

Murwinek) to  $0.25 \text{ mg}\cdot\text{dm}^{-3}$  (Lake Żońskie). Waters of Lake Czeszewskie were particularly rich in bicarbonates, sulphates and chloride anions ( $256, 367, 250 \text{ mg}\cdot\text{dm}^{-3}$  respectively), the content of anions in waters of other lakes ranged within the following limits: bicarbonates  $54\text{-}185 \text{ mg}\cdot\text{dm}^{-3}$ , sulphates  $7\text{-}323 \text{ mg}\cdot\text{dm}^{-3}$  and chlorides  $40\text{-}110 \text{ mg}\cdot\text{dm}^{-3}$  (Tables 7-10).

During *summer stagnation*, pH values for *the surface water layer* of **field lakes** ranged from 7.52 to 8.78, whereas the value of electrical conductivity ranged within the limits of  $264\text{-}1105 \mu\text{S}\cdot\text{cm}^{-1}$ . A decrease in electrical conductivity, compared with the spring season, was observed for all the analysed samples of surface water. The water transparency ranged from 0.6 to 1.8 m. For most of the field lakes, the content of iron in the surface layer decreased; the recorded values ranged from  $0.01$  to  $0.20 \text{ mg}\cdot\text{dm}^{-3}$ . The content of calcium cations ranged from 44.1 to  $171.3 \text{ mg}\cdot\text{dm}^{-3}$ , and for most lake waters the content of this ion decreased; similar tendencies were observed for the content of magnesium cations, the content of which ranged from 6.7 to  $34.1 \text{ mg}\cdot\text{dm}^{-3}$ . During summer stagnation, the content of nitrate ions considerably dropped in waters of the surface layer ( $0.002\text{-}0.025 \text{ mg}\cdot\text{dm}^{-3}$ ). The content of ammonium ions ranged from 0.08 to  $0.27 \text{ mg}\cdot\text{dm}^{-3}$  (Lakes Strzałkowo and Zbyszewickie respectively), whereas the content of total nitrogen – from 1.40 to  $7.00 \text{ mg}\cdot\text{dm}^{-3}$ . For ammonia and total nitrogen, no explicit trends in changes of their content were recorded. The content of orthophosphates(V) in the water decreased and was at the level  $0.013\text{-}0.082 \text{ mg}\cdot\text{dm}^{-3}$  (Lakes Żońskie and Zbyszewickie respectively). The content of bicarbonates ranged from 78 to  $184 \text{ mg}\cdot\text{dm}^{-3}$  and for most of the studied samples, the content of this anion was decreasing during the season of summer stagnation. Changes in the content of sulphates(VI) ( $14\text{-}318 \text{ mg}\cdot\text{dm}^{-3}$ ) and chlorides ( $35\text{-}190 \text{ mg}\cdot\text{dm}^{-3}$ ) were not so explicit (Tables 7-10).

Water reaction *of the bottom layer* in the **field lakes** ranged from pH = 7.06 to pH = 7.63 and was lower for all the lakes compared with the reaction of the surface layer. These samples were characterized by a slightly higher value of electrical conductivity compared with samples of the surface layer, from 350 to  $1129 \mu\text{S}\cdot\text{cm}^{-1}$ . The total content of iron in the layer of benthic water ranged from 0.03 to  $0.90 \text{ mg}\cdot\text{dm}^{-3}$ . For most of the lakes, waters of the benthic layer were richer in calcium ( $56.1\text{-}178.4 \text{ mg}\cdot\text{dm}^{-3}$ ) and poorer in magnesium ( $6.1\text{-}25.5 \text{ mg}\cdot\text{dm}^{-3}$ ). Ammonia nitrogen occurred in the concentrations ranging from 0.08 to  $0.89 \text{ mg}\cdot\text{dm}^{-3}$ , whereas nitrate nitrogen – from 0.002 to  $0.032 \text{ mg}\cdot\text{dm}^{-3}$ . There was a big difference in the total nitrogen content between the surface and the benthic layer; the concentrations recorded in the benthic layer were higher and ranged from 3.50 to  $19.61 \text{ mg}\cdot\text{dm}^{-3}$ . The content of orthophosphates(V) ranged from 0.005 (Lake Strzałkowo) to  $0.391 \text{ mg}\cdot\text{dm}^{-3}$  (Lake Bobrów). The concentrations of bicarbonates amounted to  $93\text{-}207 \text{ mg}\cdot\text{dm}^{-3}$  and were higher than those recorded in the surface layer; the concentrations of sulphates(VI) ranged from 30 to  $286 \text{ mg}\cdot\text{dm}^{-3}$ . The content of chlorides ranged from 23 to  $180 \text{ mg}\cdot\text{dm}^{-3}$  (Tables 7-10).

Table 7. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site		Lake Bobrów (P1)		Lake Murwinek (P2)	
	A*	B	spring circulation	summer stagnation	spring circulation	summer stagnation
pH			8.79	8.78	8.29	7.52
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A	B	323	264	772	717
			–	350	–	–
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A	B	0.21	0.01	0.23	0.01
			–	0.90	–	–
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A	B	43.1	44.1	104.2	100.2
			–	56.1	–	–
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A	B	10.3	6.7	21.9	19.5
			–	6.1	–	–
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	0.35	0.12	0.09	0.09
			–	0.08	–	–
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	1.02	0.025	1.24	0.003
			–	0.032	–	–
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	2.07	4.93	4.74	1.40
			–	9.13	–	–
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A	B	0.080	0.049	0.050	0.016
			–	0.391	–	–
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A	B	99	90	146	107
			–	140	–	–
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A	B	9	28	227	215
			–	34	–	–
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A	B	40	35	108	120
			–	23	–	–
Transparency (m)			0.5	0.7	0.4	0.6

A\* – 1 metre below the surface, B – 1 metre above the bottom



Table 8. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site		Lake Zbyszewickie (P3)		Lake Pawłowskie (P4)	
	A*	B	spring circulation	summer stagnation	spring circulation	summer stagnation
pH	A*	B	8.15	8.42	8.05	8.52
			–	7.50	–	7.37
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A	B	753	641	817	740
			–	736	–	803
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A	B	0.25	0.08	0.13	0.20
			–	0.03	–	0.41
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A	B	103.2	82.2	110.2	116.2
			–	104.2	–	122.2
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A	B	20.6	18.2	20.7	34.1
			–	17.0	–	23.1
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	0.01	0.27	0.08	0.17
			–	0.20	–	0.85
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	1.47	0.002	1.02	0.005
			–	0.002	–	0.011
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	6.37	1.40	3.12	7.00
			–	3.50	–	19.61
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A	B	0.120	0.082	0.160	0.018
			–	0.130	–	0.023
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A	B	138	78	171	134
			–	153	–	166
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A	B	31	318	209	277
			–	30	–	277
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A	B	95	105	105	120
			–	110	–	120
Transparency (m)	–	–	0.6	0.9	1.1	1.0

A\* – 1 metre below the surface, B – 1 metre above the bottom

Table 9. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site	Lake Czeszewskie (P5)		Lake Strzałkowo (P6)	
		spring circulation	summer stagnation	spring circulation	summer stagnation
pH	A* B	7.85 –	8.26 7.63	8.08 –	8.05 7.06
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A B	1257 –	1105 1129	717 –	644 724
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A B	0.08 –	0.14 0.14	0.17 –	0.05 0.07
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A B	200.4 –	171.3 178.4	101.2 –	90.2 90.2
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A B	25.5 –	28.6 25.5	18.9 –	9.7 17.0
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A B	0.18 –	0.22 0.19	0.62 –	0.08 0.89
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A B	0.723 –	0.014 0.003	1.08 –	0.002 0.002
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A B	4.92 –	2.11 3.50	7.38 –	1.40 3.50
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A B	0.100 –	0.020 0.009	0.160 –	0.020 0.005
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A B	256 –	184 207	54 –	88 93
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A B	367 –	264 55	323 –	14 40
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A B	250 –	190 180	110 –	127 130
Transparency (m)	–	1.5	1.4	1.3	1.2

A\* – 1 metre below the surface, B – 1 metre above the bottom

Table 10. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site		Lake Żońskie (P7)		Lake Czworokątne (L1)	
	A*	B	spring circulation	summer stagnation	spring circulation	summer stagnation
pH	A*	B	8.05	8.21	8.26	8.13
			–	7.57	–	7.04
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A	B	881	804	364	351
			–	862	–	472
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A	B	0.15	0.11	0.20	0.01
			–	0.08	–	0.07
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A	B	131.3	126.3	54.1	38.1
			–	134.3	–	63.1
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A	B	19.5	18.9	12.2	15.8
			–	23.1	–	11.6
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	0.04	0.21	0.62	0.30
			–	0.23	–	4.90
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	2.15	0.014	0.248	0.002
			–	0.025	–	0.003
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	4.25	4.91	3.05	3.50
			–	6.33	–	5.75
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A	B	0.250	0.013	0.031	0.018
			–	0.196	–	0.013
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A	B	185	154	207	157
			–	183	–	239
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A	B	7	201	74	35
			–	286	–	33
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A	B	100	80	28	21
			–	135	–	10
Transparency (m)	–	–	1.1	1.8	0.5	0.7

A\* – 1 metre below the surface, B – 1 metre above the bottom

Waters of **forest lakes** during *spring circulation* were characterized by a slightly alkaline and alkaline reaction (pH = 6.50-8.74). Electrical conductivity of the described lake waters was low and ranged from 152 to 424  $\mu\text{S}\cdot\text{cm}^{-1}$ . Transparency of waters ranged from 0.5 to 2.7 m. The total content of iron ranged from 0.19  $\text{mg}\cdot\text{dm}^{-3}$  in the waters of Lake Borowe to 0.43  $\text{mg}\cdot\text{dm}^{-3}$  in the waters of Lake Pniewo. The lowest content of calcium and magnesium ions was recorded in the surface waters of Lake Szamoty Duże (16.0 and 3.0  $\text{mg}\cdot\text{dm}^{-3}$  respectively), the highest content of calcium cations – in the waters of Lake Sumile (60.1  $\text{mg}\cdot\text{dm}^{-3}$ ), and magnesium – in the waters of Lake Czworokątne (12.2  $\text{mg}\cdot\text{dm}^{-3}$ ). The highest content of ammonium ions was recorded in the waters of Lake Szamoty Duże (1.24  $\text{mg}\cdot\text{dm}^{-3}$ ). The highest concentration of nitrate ions occurred in the waters of Lake Hanki (0.678  $\text{mg}\cdot\text{dm}^{-3}$ ), the remaining lakes were characterized by a much lower content of these ions (0.023-0.508  $\text{mg}\cdot\text{dm}^{-3}$ ), whereas the total content of nitrogen ranged from 2.53  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Sumile) to 11.92  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Borowe). In the case of orthophosphates(V), the lowest concentration was recorded in the waters of Lake Pniewo (0.016  $\text{mg}\cdot\text{dm}^{-3}$ ), the highest – in the surface water layer of Lake Czworokątne (0.031  $\text{mg}\cdot\text{dm}^{-3}$ ). The content of bicarbonates was highly diverse and ranged from 6  $\text{mg}\cdot\text{dm}^{-3}$  in Lake Pniewo to 207  $\text{mg}\cdot\text{dm}^{-3}$  in Lake Czworokątne. Also the content of sulphates(VI) was heterogeneous and ranged from 8 to 209  $\text{mg}\cdot\text{dm}^{-3}$ . The recorded concentrations of chlorides were the least heterogeneous and ranged from 5 to 35  $\text{mg}\cdot\text{dm}^{-3}$  (Tables 10-13).

During *summer stagnation*, pH values of *surface water* increased (pH = 6.78-9.26) for most of the lakes, and values of water electrical conductivity decreased (153-351  $\mu\text{S}\cdot\text{cm}^{-1}$ ) compared with values obtained in the spring season. For the majority of cases, water transparency decreased (0.5-1.8 m). The total content of iron increased only in the water of Lake Sumile and amounted to 0.25  $\text{mg}\cdot\text{dm}^{-3}$ , whereas in other lakes it decreased considerably and ranged from 0.01 (Lakes: Czworokątne, Krąpsko Małe and Borowe) to 0.04  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Hanki). The concentrations of calcium ions ranged from 17.0  $\text{mg}\cdot\text{dm}^{-3}$  in the water of Lake Szamoty Duże to 60.1  $\text{mg}\cdot\text{dm}^{-3}$  in the surface water of Lake Hanki, whereas the content of magnesium ranged from 4.3 to 15.8  $\text{mg}\cdot\text{dm}^{-3}$ . For most of the samples, the content of ammonium ions decreased during the summer stagnation (0.12-0.30  $\text{mg}\cdot\text{dm}^{-3}$ ), whereas the content of nitrate nitrogen(V) decreased in all the analysed water samples (0.002-0.158  $\text{mg}\cdot\text{dm}^{-3}$ ). The total content of nitrogen in the analysed surface waters ranged from 2.10 to 5.61  $\text{mg}\cdot\text{dm}^{-3}$ . The concentration of orthophosphates(V) fluctuated within the range from 0.001  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Borowe) to 0.026  $\text{mg}\cdot\text{dm}^{-3}$  (Lake Sumile). For most of the lakes, the concentrations of bicarbonates decreased compared with the season of spring circulation (21-157  $\text{mg}\cdot\text{dm}^{-3}$ ), whereas the content of chlorides ranged from 10 to 72  $\text{mg}\cdot\text{dm}^{-3}$ . The content of sulphates (VI) ranged from 19 to 255  $\text{mg}\cdot\text{dm}^{-3}$  (Tables 10-13).

For all the studied lakes, waters of *the bottom layer* were characterized by lower pH (5.91-8.27) compared with the surface layer and for most of them – by higher electrical conductivity (150-556  $\mu\text{S}\cdot\text{cm}^{-1}$ ). Most of the samples were characterized by a higher concentration of total iron, ranging from 0.01 to 0.9  $\text{mg}\cdot\text{dm}^{-3}$ . Similar differences in the content were recorded for calcium ions, the content of which ranged from 16.0 to 72.1  $\text{mg}\cdot\text{dm}^{-3}$ . The recorded concentrations of magnesium were within the range of 3.7-11.6  $\text{mg}\cdot\text{dm}^{-3}$ .

For most of the samples, the content of ammonia nitrogen was higher compared with the surface layer, and it was particularly high in the water of Lake Czworokątne (40.90  $\text{mg}\cdot\text{dm}^{-3}$ ) and Lake Sumile (6.21  $\text{mg}\cdot\text{dm}^{-3}$ ). The content of nitrate nitrogen(V)

ranged from 0.002 to 0.012 mg·dm<sup>-3</sup>. As in the case of ammonia nitrogen, the highest content of total nitrogen was recorded in the water of Lake Sumile (17.01 mg·dm<sup>-3</sup>); in the other lakes, the water content of nitrogen ranged from 1.40 to 7.71 mg·dm<sup>-3</sup>. The concentrations of orthophosphates(V) were very different and ranged from 0.007 to 3.261 mg·dm<sup>-3</sup>. For most of the water samples collected from the benthic layer, the content of bicarbonates was higher (21-239 mg·dm<sup>-3</sup>) compared with the surface layer. The content of sulphates(VI) fluctuated within the range from 30 to 251 mg·dm<sup>-3</sup>, whereas the content of chlorides – from 10 to 50 mg·dm<sup>-3</sup> (Tables 10-13) [14].

Chemical composition of the water differed between the studied lakes and depended on the season, sample collection sites and the catchment area management. The influence exerted by the sampling time (spring-summer) and sampling location (the surface layer versus the benthic layer) is obvious and consistent with the limnological knowledge. For instance, the results obtained for the determination of the content of nitrates(V) and orthophosphates(V) – higher in the spring and lower in the summer, are a consequence of generally known biological and chemical processes occurring in the pelagic zone in the annual cycle [20].

In order to determine the influence of a catchment area on the chemical composition of waters, the statistical analysis was performed on the results with the two-way analysis of variance (factors: water of lakes with an agricultural catchment area and water of lakes with an forest catchment area). The significance of differences between the parameters was assessed with Tukey's test at the level of  $p < 0.05$ . The performed statistical analysis proved that not all parameters of the physicochemical composition of the water significantly depend on the land use in catchment areas of the lakes. Average values and LSD values were collated in Table 14 only for the parameters for which significant differences were found. For the other analysed parameters, the differences were not significant.

Among the analysed water parameters, values of only four of them (electrical conductivity, the content of chlorides, calcium and magnesium) significantly depended on the catchment land use, irrespective of the time and the water layer from which the water samples were collected for the analyses. Additionally, surface waters of the lakes in the agriculturally exploited catchment area contained significantly more nitrates(V) and orthophosphates(V) in spring, compared with waters of the lakes in the forest catchment area. Information about the lack of significant differences in the content of ammonia nitrogen and total nitrogen in the waters of the lakes with diverse catchment land use is important for the evaluation of influence exerted by the catchment area on the quality of water in the lakes. Although the content of ammonia nitrogen and total nitrogen was higher in the waters of the lakes located in the forest catchment area, the differences were not significant. Probably this is a consequence of a high variability in the content of these elements.

Water electrical conductivity is determined mainly by the total concentration of ions. Throughout the year, the content of ions Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, and thus ions that participate in the biological cycles to a small extent only, was higher in the water from the agricultural catchment area compared with the water from the forest catchment area. The lack of significant differences in the content of nitrates and orthophosphates in the summer should be related to the use of these nutrients in the production of phytoplankton biomass [20].

Table 11. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site		Lake Krapsko Mate (L2)		Lake Sumile (L3)	
	A*	B	spring circulation	summer stagnation	spring circulation	summer stagnation
pH	A*	B	8.20	8.03	8.74	9.26
			–	7.30	–	7.23
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A	B	328	312	424	341
			–	354	–	556
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A	B	0.21	0.01	0.21	0.25
			–	0.02	–	0.01
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A	B	58.1	52.1	60.1	51.1
			–	64.1	–	72.1
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A	B	6.1	6.1	9.1	5.5
			–	4.9	–	9.7
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	0.29	0.14	0.18	0.19
			–	0.78	–	6.21
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	0.023	0.004	0.429	0.158
			–	0.003	–	0.008
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	B	2.82	4.72	2.53	2.26
			–	2.80	–	17.00
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A	B	0.024	0.020	0.027	0.026
			–	0.065	–	3.261
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A	B	167	156	90	65
			–	184	–	68
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A	B	8	19	170	125
			–	39	–	125
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A	B	6	30	35	72
			–	15	–	50
Transparency (m)	–	–	1.5	1.1	1.2	1.8

A\* – 1 metre below the surface, B – 1 metre above the bottom

Table 12. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site	Lake Hanki (L4)		Lake Borowe (L5)	
		spring circulation	summer stagnation	spring circulation	summer stagnation
pH	A*	8.40	8.93	8.21	8.54
	B	–	7.13	–	8.27
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A	341	298	289	255
	B	–	315	–	234
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A	0.27	0.04	0.19	0.01
	B	–	0.05	–	0.04
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A	56.1	60.1	48.9	45.1
	B	–	62.1	–	46.1
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A	6.7	6.1	6.8	9.1
	B	–	4.9	–	7.3
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	0.36	0.16	0.27	0.12
	B	–	0.64	–	0.14
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	0.678	0.002	0.023	0.009
	B	–	0.008	–	0.002
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A	6.98	2.10	11.92	5.61
	B	–	4.91	–	2.80
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A	0.025	0.010	0.017	0.001
	B	–	0.050	–	0.026
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A	134	143	148	137
	B	–	151	–	138
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A	70	33	21	23
	B	–	43	–	30
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A	20	20	5	10
	B	–	22	–	18
Transparency (m)	–	1.1	1.0	2.7	1.6

A\* – 1 metre below the surface, B – 1 metre above the bottom



Table 13. Physicochemical properties of water in the studied lakes [14]

Parameter	Sample collection site		Lake Szamoty Duże (L6)		Lake Pniewo (L7)	
	A*	B	spring circulation	summer stagnation	spring circulation	summer stagnation
pH	A*	B	7.35	8.83	6.50	6.78
	B		–	7.09	–	5.91
Electrical conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	A		152	153	169	166
	B		–	150	–	183
Total iron ( $\text{mg Fe}\cdot\text{dm}^{-3}$ )	A		0.41	0.03	0.43	0.02
	B		–	0.02	–	0.90
Calcium ( $\text{mg Ca}\cdot\text{dm}^{-3}$ )	A		16.0	17.0	19.0	22.0
	B		–	16.0	–	23.0
Magnesium ( $\text{mg Mg}\cdot\text{dm}^{-3}$ )	A		3.0	4.3	3.0	5.5
	B		–	5.5	–	3.7
Ammonia nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A		1.24	0.29	0.10	0.16
	B		–	0.27	–	0.16
Nitrate nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A		0.508	0.002	0.140	0.004
	B		–	0.002	–	0.012
Total nitrogen ( $\text{mg N}\cdot\text{dm}^{-3}$ )	A		8.21	2.80	2.94	4.20
	B		–	1.40	–	7.71
Orthophosphates ( $\text{mg P}\cdot\text{dm}^{-3}$ )	A		0.024	0.013	0.016	0.007
	B		–	0.050	–	0.007
Bicarbonates ( $\text{mg HCO}_3\cdot\text{dm}^{-3}$ )	A		59	55	6	21
	B		–	22	–	21
Sulphates ( $\text{mg SO}_4\cdot\text{dm}^{-3}$ )	A		209	38	23	255
	B		–	58	–	251
Chlorides ( $\text{mg Cl}\cdot\text{dm}^{-3}$ )	A		5	11	22	20
	B		–	10	–	40
Transparency (m)	–	–	1.1	0.5	1.6	0.9

A\* – 1 metre below the surface, B – 1 metre above the bottom

Table 14. Water quality parameters for the studied lakes (mean values) [14]

Lakes	Electrical conductivity $\mu\text{S}\cdot\text{cm}^{-1}$	P-PO <sub>4</sub> <sup>3-</sup>	N-NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
		mg·dm <sup>-3</sup>				
The surface layer – spring						
Field	786	0.131	1.24	115	113	19.6
Forest	295	0.023	0.29	17	45	6.7
LSD p < 0.05	241	0.054	0.43	53	41	4.7
The surface layer – summer						
Field	702	0.031	0.009	111	104	19.4
Forest	268	0.014	0.026	26	41	7.5
LSD p < 0.05	216	ns	ns	43	35	8.6
The benthic layer – summer						
Field	760	0.109	0.013	117	112	18.7
Forest	323	0.496	0.005	24	50	6.7
LSD p < 0.05	226	ns	ns	41	36	5.8

ns – non-significant differences

The differences in the content of only certain water elements, confirmed by the statistical analysis, indicate that their source may come from agricultural activity in the catchment areas. Nitrates(V), phosphates(V) and chlorides constitute the main components of mineral fertilizers. Saltpetre, superphosphates, potash salt are the main forms of mineral fertilizers, commonly applied in agriculture. Application of mineral fertilizers in autumn together with comprehensively performed agricultural treatments can induce the excessive run-off with surface waters into the lakes in spring, which may account for the obtained relationships. Seasonal application of calcium-magnesium fertilizers can be the source of calcium and magnesium ions in the waters of lakes situated in the catchment area with agricultural land use, and on the other hand – they may come from displacement of these ions from the soil sorption complex, which is a consequence of applying the physiologically acid fertilizers or the progressive process of soil acidification. Management of fertilizers in the Polish agriculture during the last 10 years is difficult to assess. On the one hand, due to economic reasons, there was a considerable reduction in the consumption of fertilizers, on the other hand, they are often applied unilaterally, which results in adverse changes in the abundance and the sorption complex of soil. In view of the obtained results and in terms of lake water protection, it is necessary to support the idea of sustainable agriculture, where fertilization systems are considered on the basis of current demands of cultivated plants for fertilizer components. This will eliminate the excess application of fertilizers, particularly in autumn, and will introduce the principle of multiple fertilization during the growing season when lands are covered with crops.

In order to confirm that the chemical composition of water in the lakes is determined by a catchment management system, the statistical cluster analysis was applied using Ward's method [89]. The cluster analysis was applied to the results of water analyses performed with the method of Kudelska and co-authors [49]. The following parameters were included in the first stage of the analysis: transparency,

specific conductivity and the content of orthophosphates(V), ammonia nitrogen, mineral nitrogen (the total of ammonia and nitrate(V) nitrogen) and total nitrogen. The thus obtained diagram is presented in Figure 18.

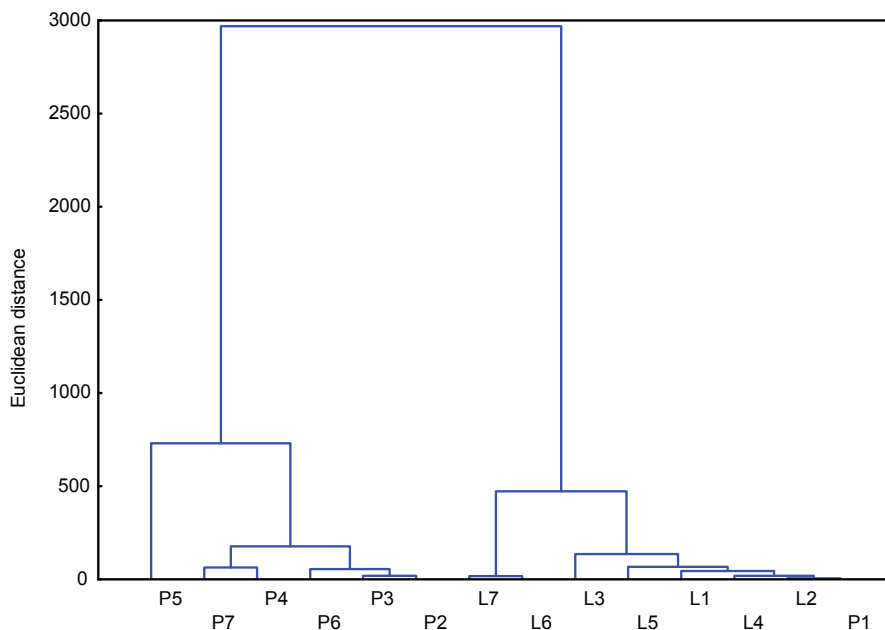


Fig. 18. Clustering of lakes based on the results of water analysis (parameters selected according to Kudelska *et al.* [49]) [14]

As a result of the cluster analysis, waters in the studied lakes were divided into two groups: waters of lakes in the agricultural catchment area (P) and waters of lakes in the forest catchment area (L). The only exception is Lake Bobrów (P1), the water of which was classified within the group of lakes with the forest catchment area. Based on the results of corresponding analyses, the waters of the studied lakes can be classified as follows:

- water quality class II: Lake Borowe (L5), Lake Pniewo (L7),
- water quality class III: Lake Czeszewskie (P5), Lake Strzałkowo (P6), Lake Hanki (L4), Lake Czworokątne (L1), Lake Krąpsko Małe (L2), Lake Szamoty Duże (L6), Lake Sumile (L3),
- outside the water quality classes: Lake Murwinek (P2), Lake Żońskie (P7), Lake Bobrów (P1), Lake Pawłowskie (P4), Lake Zbyszewickie (P3).

At the second stage, the cluster analysis was applied to a bit different set of water quality parameters, namely those parameters for which the previously performed and discussed analysis of variance revealed significant differences between the waters of lakes with different catchment land use: electrical conductivity, the content of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , and those were mean values for the samples collected from the surface layer on two different dates. The result of clustering is presented in Figure 19.

Also in this case, an almost identical result of clustering was obtained as previously – the division into lakes with agricultural and forest catchment land use. Lake Bobrów is a unique lake, which has been placed in the group of lakes with forest catchment land use.

It is evident from the performed researches that compared with waters of forest lakes, waters of field lakes are richer in orthophosphates(V), nitrates(V), chlorides, calcium and magnesium. They are also characterized by a higher electrical conductivity [14].

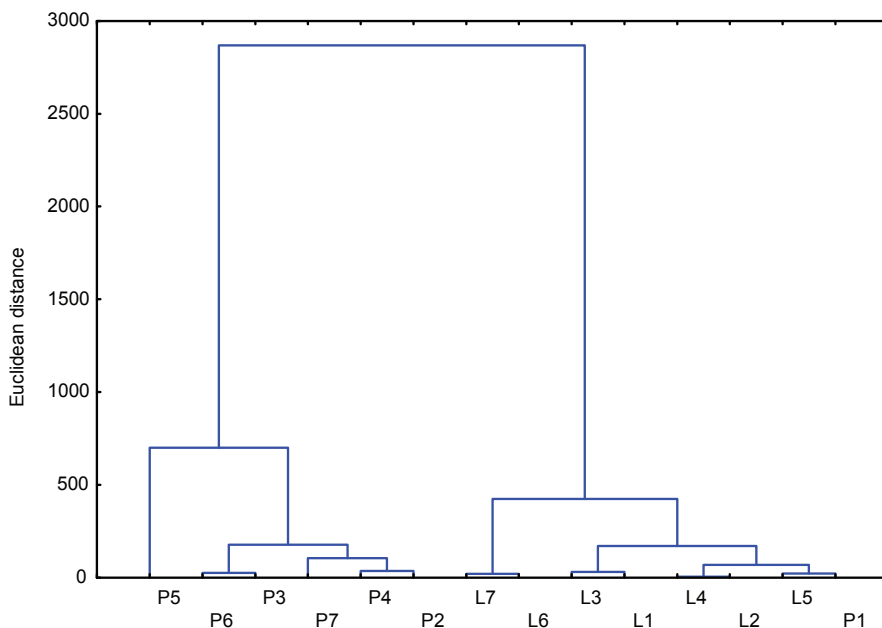


Fig. 19. Clustering of lakes based on the results of water analysis (parameters selected according to the author's selection) [14]

### 3. BOTTOM SEDIMENTS

#### 3.1. ACCUMULATION OF ORGANIC MATTER

The primary source of organic matter in the sediments is specific detritus from plants growing in lakes and the surrounding land. The sources of organic matter and the processes that modify it during incorporation into sediments are presented in Figure 20. Almost the whole organic matter in the sediments is of plant origin, only ca. 10% is composed of remains of animal origin. Based on the biochemical composition, plants can be divided into two important geochemical groups: (i) nonvascular plants, which do not have tissues containing cellulose and lignin, e.g. simple algae and (ii) vascular plants, which have these tissues, such as grass, shrubs and trees. Vascular plants occur on land and in shallow parts of lakes as emergent vegetation enrooted in the bottom. Relative contributions of these two groups of plants are affected by the morphology of a lake, topography of a catchment area and abundance of a lake, as well as vegetation of a catchment area. The origin of the sediment cover can range from mainly algal in some lakes to mainly terrestrial in others. Bacteria and other microorganisms occurring in the water, lacustrine sediments and in the soil of a catchment area continually modify and degrade the organic matter of aquatic and terrestrial origin. Bacteria biosynthesize characteristic forms of organic matter by decomposing the previously formed organic matter, which developed from plants and animals living in a lake and in a catchment area. Organic matter, such as pollen, can be delivered to a lake by wind from outside a local catchment area.

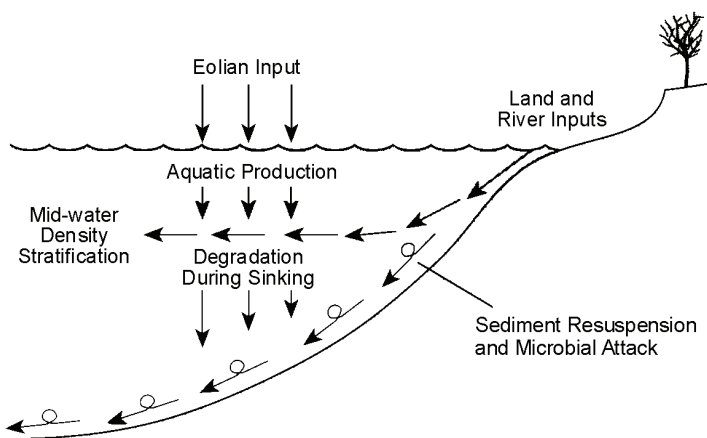


Fig. 20. The sources of organic matter and the processes that modify it during incorporation into bottom sediments [62]

The eolian component constitutes a small percentage of the whole organic mixture. It can contain, however, characteristic components, which are the potential source of information for paleolimnological and paleoclimatic studies. Evaluation of organic matter sources in oligotrophic Lake Michigan represents an example of a relative contribution of material with miscellaneous origin, as it was found that 90% of organic carbon in the lake waters comes from the primary production, 5% is transported by rivers, the remaining 5% is delivered with the precipitation and the air. Particular

fractions are susceptible to selective degradation and therefore their quantitative relations in sediments seldom stay intact [2].

Lakes are depositional environments for limnic, telmatic and in some cases also terrestrial sediments. Accumulation of the aforementioned groups of sediments proceeds during the sedimentation and sedimentation process.

The process of sedimentation consists in accumulation of the material brought from outside the lake basin (allochthonous material) and formed in the pelagic zone (autochthonous material). The matter accumulated under the water can be subject to diagenesis, which leads to considerable transformations of initial properties of the newly developed sediments. All phenomena that transform the accumulated matter do not change, however, the depositional origin of sediments or any of their components.

The second possibility of sediment formation is a specific way the autochthonous matter accumulates, which is called sedimentation. In the process of organic matter accumulation, layers of biogenic sediments develop from the biomass of vegetation enrooted in the sediment. This way of sediment formation occurs due to depositional activity of root systems of peat-forming plants, specialized in the accumulation of substantial amounts of plant matter. Roots and underground shoots of peat-forming plants can penetrate in a specific way through the surface layers of the previously accumulated organic matter, and thus contribute to the increase of its thickness.

In young and large lakes, accumulation of bottom sediments proceeds mainly via sedimentation. The process of sedimentation is of minor significance in such lakes, limited to the external part of the littoral zone. Gradually, together with ageing of water reservoirs and together with their progressive shallowing, sedimentation becomes a dominant process. The process of excluding sedimentation and replacing it entirely with sedimentation takes place on a peat bog, which takes over the top of a former lake filled up with sediments. Each of the accumulation stages leaves abundant sediments in water bodies with specific lithological characteristics and petrographic composition. Components that come from the biotic sphere of lake and peat-bog ecosystems are of particularly great significance for the identification of sediments and determination of their genesis.

Water reservoirs and their surrounds comprise three depositional environments: aquatic (limnic), amphibious (telmatic) and terrestrial (terrestrial). Three groups of biogenic sediments develop there: gyttja (representing limnic sediments formed in the process of sedimentation), peat developed from reed beds (telmatic sediments) and the remaining types of peat accumulated in the deposits of terrestrial origin. Both groups of peat deposits result from the process of sedimentation.

**Limnic (lacustrine) depositional environment** includes the water column of the pelagic zone, both its euphotic or aphotic parts, the demersal part of the profundal zone and the deeper part of the littoral zone. In most of the lakes of the temperate climate zone, the borderline separating the depositional accumulation of biogenic sediments from sediments developed in the sedimentation process runs through the littoral zone. At the same time the zone separating these two main processes of biogenic accumulation constitutes the morphological and functional borderline of a peat bog, which runs within the morphological area of a present lake. The remaining part of the littoral zone situated within the water surface limits, even after reaching the lowest water level, is an integral part of the limnic depositional environment, despite the fact that frequent bottom sediments are morphologically similar to peat deposits, yet the parent plant communities of these sediments – coarse detritus gyttja – are sublittoral phytocoenoses (the lake's slope).

**Telmatic depositional environment** is located within the littoral zone of a lake and covers a part of the littoral zone (eulittoral) within the water surface between the highest and the lowest water level. Eulittoral is an important biotope, overgrown by many plant communities. Most often, they form a few zones of rush vegetation, some of which are characterized by a considerable peat-forming activity. The existence in the conditions of a changing water level induced the development of two adaptive formations in the littoral vegetation, which respond to water-level fluctuations in a different way. One can distinguish two types of plants: those capable of immersing and those capable of emerging.

Forms of submerged plants do not respond to water fluctuations, because they are fixed in the solid substrate with systems of underground parts, and they remain more or less immersed depending on the water level. The group of submerged plants comprises reed and canary grass beds, as well as most of the tall sedge communities. The response of emergent forms is different, they are not flooded but instead, they rise or fall depending on the water level. In this way, at least the surface part of the depositively active part of phytocoenoses preserves the same water level all the time, irrespective of the water-surface fluctuations in a lake. Peat-forming communities of short sedge and sedge-moss plant communities are the example of emergent forms.

**Terrestrial (terrestic) depositional environment** is situated outside the littoral zone. The depositional area of this environment is no longer situated within the range of lake waters or on the minerogenic substrate of the land – it comprises the terrain capable of accumulating the biogenic deposits. Usually they are a residuum of the previous filling of a lake basin with deposits and are often referred to as “terrestrialization” of the initial water surface. This group of depositional environments includes also areas adjacent to the littoral zone, which become marshy under the influence of a nearby water body and subterranean waters [87].

### **3.2. TRANSFORMATIONS OF ORGANIC MATTER DURING DEPOSITION**

Diversity in the occurring processes brings about changes in properties of organic matter in a relatively short time, between its source and deposition at the lake bottom. Degradation during deposition is the main process. The research carried out in Lake Michigan revealed that only 6% of carbon produced in the process of photosynthesis in the surface water of the southern part of the lake reaches the surface of the sediment situated 100 m below. About 85% of carbon is oxidized before it leaves the epilimnion [21]. In the case of shallower lakes, organic matter can be exposed to oxidation in the water column for a shorter time. Consequently, such reservoirs usually have sediments richer in organic matter. Oxidation and degradation of organic matter still continue after its deposition at the bottom. Sediment resuspension is also important, because organic matter is again exposed to microbiological oxidation in the water column [21, 60, 63]. Resuspension of sediments is usually greater in large, well mixed water reservoirs. Bioturbation, or biological mixing of surface sediments, also prolongs the exposure of organic matter to oxidation and increases the extent of degradation due to consumption by benthic fauna. The depth of bioturbation in Great Lakes comes to ca. 10 cm [41, 72]. In lakes with seasonal or permanent deoxidation of benthic water, bioturbation is less intensive or does not occur at all, because bottom animals require dissolved oxygen for respiration. Many lakes of the temperate zone undergo periods of hypoxia during

summer stagnation and sediments of these lakes are characterized by a higher content of organic matter as compared with lakes permanently oxygenated. Organic matter located below the bioturbation zone is exposed to transformations caused by anaerobic bacteria. Waters of many lakes contain too little sulphates necessary for the process of reduction, however the processes of degradation are continued by methane bacteria if the deposited organic matter contains the sufficient amount of labile materials, indispensable for maintaining the microbiological activity. Less active forms of organic matter begin to dominate in the sediment when more reactive forms are used by microorganisms and animals feeding on sediment. Components of aquatic sediments are more sensitive to processes of microbiological degradation as compared with sediments coming from terrestrial sources. Consequently, the organic matter in the lacustrine deposits contains a relatively large and relatively non-reactive fraction of terrestrial origin. Moreover, humus substances and lipids are less reactive compared with amino compounds and carbohydrates, and therefore their contribution in sediments increases together with the increasing depth [42]. In older deposits, only the most resistant forms of the primary mixture remain. During the whole cycle of transformations, the residues of organic matter synthesized by microorganisms are added to the mixture, some of them can be modified or decomposed, the others – preserved. Organic matter is the end result of these complex processes with the composition often different from organic matter produced in a lake and a catchment area.

### **3.3. INDICATORS OF SOURCES AND TRANSFORMATIONS OF ORGANIC MATTER**

The accumulated matter of bottom sediments in lakes reflects the types and the amounts of materials from primary sources and the extent of transformations and degradation of the initial material. Sources and transformations of organic matter change both geographically and in time. Although the record of sediment accumulation for every lake is usually unique, the researches on different lakes enabled to acquire the knowledge about some factors affecting the content of organic matter in bottom sediments.

Values of the C:N ratio in sediments are determined on the basis of chemical composition of organic material deposited at the lake bottom. Nonvascular aquatic plants are characterized by narrow values of the C:N ratio ranging from 4 to 10, whereas for terrestrial vascular plants, which contain cellulose, the value of this ratio comes to 20 and more (Table 15, 16). Sediments for which the contribution of organic matter originating from terrestrial plants is relatively small compared with the contribution of organic matter produced in the water column, e.g. Lakes Walker and Michigan, are characterized by a lower value of the C:N ratio compared with lakes supplied with considerable amounts of detritus coming from vascular plants, e.g. Lakes Mangrove and Bosumtwi (Table 15). The ratio values of 13-14 for the surface sediments indicate the contribution of remains of vascular and nonvascular plants in the sediment, which is characteristic of most of the lakes. The broad range of the C:N ratio in sediments can indicate a considerable contribution of organic material coming from decomposition of vascular plants' remains. Selective degradation of organic matter components during early diagenesis can modify the chemical composition, and at the same time the C:N ratio of organic matter in the sediment. Values of the C:N ratio for contemporary samples of wood are higher as compared with wood that was buried in



the sediment (Table 15). Sediment particles deposited at the bottom are characterized by the C:N ratio equal to 9, but particles of the resuspended sediment – to 8. A decline in the values of the C:N ratio was also observed in the soil [77] and this is related to the microbiological immobilization of nitrogenous material, which accompanies the mineralization of carbon. These changes in the chemical composition of the sedimentary organic matter are usually not large, but they blur the initial differences in C:N between vascular and nonvascular plants. The comparison of values of C:N ratios for the organic matter of phytoplankton (the surface), the content of sediment traps (placed at a depth of about: 17, 37, 80, 120 and 140 m) and the surface sediment in Lake Michigan indicates that values of the C:N ratio are a valuable source of information.

Table 15. Atomic C:N ratios of various plants and for bottom sediments of water reservoirs [62]

Type of samples	C:N	References
Terrestrial plants		
fresh, spruce wood	546	[34]
spruce wood, 2500 years old	541	[34]
fresh wood of red alder	264	[34]
wood of red alder, 2500 years old	106	[34]
fresh leaves of alder	38	[57]
Aquatic plants		
plankton of Lake Pyramid	6	[58]
plankton of Lake Michigan	7	[59]
plankton of Lake Walker	8	[57]
<i>Asterionella formosa</i>	9	[11]
<i>Chlamydomonas sp.</i>	7	[11]
plankton of Lake Biwa (mixed)	6-7	[67]
Sediment samples		
surface sediment, Lake Biwa	6	[61]
fixed sediment, Lake Michigan	9	[63]
surface sediment, Lake Michigan	8	[58]
resuspended sediment, Lake Michigan	8	[63]
surface sediment, Lake Walker	8	[59]
surface sediment, Lake Pyramid	9	Meyers [unpublished data]
surface sediment, Lake Baikal	11	[70]
surface sediment, the Coburn Pond	12	[36]
surface sediment, Lake Mangrove	13	[33]
surface sediment, Lake Bosumtwi	14	[82]

Table 16. Values of the C:N ratio for some types of litter [92]

Organic matter	C:N	Organic matter	C:N
Elm (different species)	23-25	European rowan	54
Alder (different species)	16-19	Goat willow	37
Ash	24	Birch	45
Hornbeam	27	Oak (different species)	40-53
Hazel	28	Beech	45
Linden	37	Spruce	48
Sycamore	51	Pine	65
Maple-aspens	56	Larch	77

Although the content of organic carbon in the plankton biomass is 10-times higher than in the organic material of the sediment, no differences in the values of the C:N ratio were recorded in this material (Fig. 21). A significant change in the value of the C:N ratio occurs during the deposition of organic matter and this is related to the observed changes in the composition of biomarkers, which indicate selective losses of algal-origin elements in the upper part of the water column and a considerable “lateral” inflow of organic matter of algal origin at greater depths. These changes reflect differentiation of diagenetic processes at different depths [61].

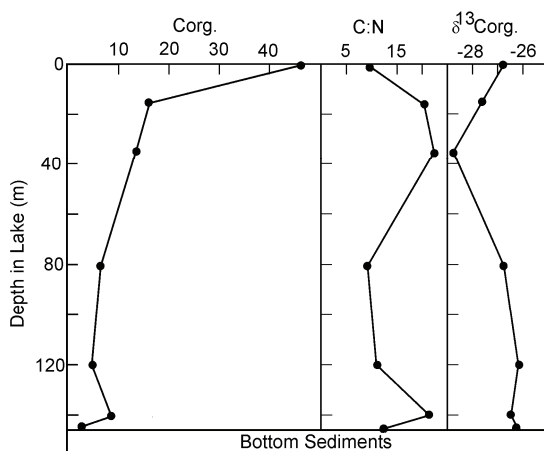


Fig. 21. The content of organic carbon, values of the atomic C:N ratio and values of  $\delta^{13}\text{C}_{\text{org}}$  for phytoplankton, the content of traps and surface sediment in Lake Michigan [60]

Peat deposits that develop in the telmatic zone are characterized by different properties, which result from the chemical composition of plants that build the sediment. It is noteworthy that the content of nitrogen is relatively small together with a high percentage contribution of oxygen (Table 17). This material is characterized by a broad range of the C:N ratio – on average 45.6 (15.4-99.2) [52].

### 3.4. CLASSIFICATION OF BOTTOM SEDIMENTS

The systematics of sedimentary rocks places the lacustrine sediments within three groups of rocks: carbonate, rocks of chemical origin and clastic rocks.

Quaternary organic rocks include peat deposits and carbonate-free gyttja (detritus). Rocks of chemical origin include carbonate (lacustrine chalk and calcareous gyttja) and ferruginous sediments. The group of clastic rocks comprises medium-clastic rocks (sands) and fine-clastic rocks (mud and clays). Bottom sediments, however, seldom form homogeneous formations built of one group of the rocks as in most of them a mixture of all three rock groups prevails. At the same time, proportions of their content vary a lot, which is the main cause of heterogeneity of both – their physicochemical properties and the size in typological and classification terms.

Table 17. Chemical composition of peat deposits (in % by weight of dry ash-free matter) [86]

Type	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
Sphagnum peat	48-53	5.0-6.1	40-46	0.5-1.0	0.10-0.20
Decomposed Sphagnum peat	56-58	5.5-6.1	34-49	0.8-1.2	0.10-0.30
Strongly decomposed Sphagnum peat	59-63	5.1-6.1	31-34	1.0-2.7	0.20-0.50

Many systems of classification and typology base their criteria on proportions of basic components of the aforementioned sedimentary rocks. The main sediments components:

- mineral components of abiotic origin – terrigenous (from outside a lake) products of mechanical weathering, mechanical denudation, brought to a lake in different ways. Coarse-, medium- and fine-grained quartz sands play the dominant role among medium-clastic formations (arkosic sands occur in smaller quantities). The mineralogical composition of the fine-clastic fraction is similar to the sandy fraction, in which quartz usually dominates, but also feldspars may occur. The finest fraction is composed of clay minerals;
- mineral components of biotic origin – carbonates, silica and iron compounds. Calcium carbonate – calcite dominates among carbonate elements. It is produced from calcium bicarbonate during the process of assimilation in aquatic plants (both algae and macrophytes). Calcium carbonate is precipitated both in the littoral zone and in the euphotic zone within the pelagic zone. In the case of a deeper water column, calcium carbonate produced in the euphotic zone and sinking into deep waters of the aphotic zone can be transformed again into a soluble bicarbonate as a result of influence exerted by carbon dioxide, which is accumulated in the deep part of the pelagic zone. Carbonates include calcareous exoskeletons of animals or their fragments, and shells of molluscs or their fragments.

Biogenic silica (opal) saturates cell walls of some algae (diatoms) and their spores, as well as forms e.g. spicules in sponges. Moreover, biogenic silica encrusts cell walls of terrestrial and amphibious vascular plants (horsetails), and can also accumulate inside of some cells.

Biogenic iron hydroxide (limonite) – usually forms concretions or thin layers of meadow ore; their fine-crystalline forms may constitute an admixture of many deposits responsible for their rust-colour.

Organic components of plant or animal origin – contain plant residues of different sizes, as well as plant fragments preserved as a whole, usually generative parts of plants of smaller sizes. The group includes underground and above-ground fragments of vegetative parts (roots, rhizomes, wood) and generative parts (fruits, seeds, sporomorphs, colonies and coenobia of algae). Organic matter of animal origin includes chitinous exoskeletons of plankton and benthic crustaceans (cladocerans – *Cladocera*, insects *Chironomidae* and *Coleoptera*), and less frequently osteological fragments of vertebrates. Humic substances that develop in bottom sediments are an important component of this fraction.

There are a number of classifications, in which efforts were made to systematize the sediments in the most comprehensible way. It is necessary to mention here the descriptive method of Troels-Smith [88], where the characterization of sediment can be presented in words and in the form of letter-numerical diagnostic formulas. The advantage of the formulas is a concise description and their comparability.

Significant researches on bottom sediments of Polish lakes were undertaken in the 1930s on dozens of lakes in the Region of Suwałki. Based on these researches, Stangenberg [79] distinguished 4 types of lacustrine sediments according to the dominant (more than 50%) contribution of the sediment component, and in the case of a few components – the contribution from ca. 30%:

- silicate sediment – apart from the dominant (more than 50%) silicate content, organic matter and calcium carbonate can constitute up to 30% of the sediment material, and the content of iron in the form of  $\text{Fe}(\text{OH})_3$  comes on average to 6%,
- organic sediment – organic matter dominates (>50%), and silicates and calcium carbonate occur in different quantities. The author also includes dy within the described type of sediments, and thus points to difficulties in their identification by means of chemical criteria,
- calcareous sediment – calcium carbonate dominates (>50%), the contribution of organic matter – up to 35% and silicates – up to 30%,
- mixed sediments are characterized by the more or less identical content of main components.

Classification of limnic sediments by Markowski [55] distinguishes three types of sediments: organic, carbonate and mineral, grouped in ten lower units at the level of kind:

- a) the type of **organic** sediment includes three subtypes:
  - algal gyttja with the content of organic matter above 80%,
  - coarse detritus gyttja with the content of organic matter of 60-90%,
  - fine detritus gyttja with the content of organic matter of 35-75%;
- b) the type of **carbonate** sediment includes four subtypes:
  - lacustrine chalk, with the content of  $\text{CaCO}_3$  above 80% and organic matter – less than 20%,
  - calcareous gyttja,  $\text{CaCO}_3$  – 50-80%, organic matter – below 40%,
  - detrital – calcareous gyttja,  $\text{CaCO}_3$  – 20-50%, organic matter – more than 30%, and the contribution of mineral elements – less than 40%,
  - clayey-calcareous gyttja, the content of  $\text{CaCO}_3$  within the range of 20-50%, mineral elements below 60%, and organic matter up to 30%;
- c) The type of **mineral** sediment includes three subtypes:
  - clayey gyttja,
  - sandy-clayey gyttja,
  - diatomaceous-clayey gyttja.

The aforementioned subtypes of mineral sediments have identical ranges of the content:  $\text{CaCO}_3$  up to 20%, organic matter from 5 to 35% and mineral elements above 65% [87].

### 3.5. CHARACTERISTIC OF BOTTOM SEDIMENTS

Bottom sediments collected in the littoral zone and in the profundal zone (within the area of the maximum depth) constituted the study material. Sample collection sites are presented on maps included in Chapter 2 (Fig. 2-15). Sediments were collected from the layer of 0-20 cm with Ekman's catcher. After bringing the samples to the air-dry state, sediment samples were ground in a mortar and sieved through a sieve with a mesh diameter of 1 mm.

The following parameters were identified in the analysed material:

- the content of total carbon (TC) and inorganic carbon (IC) by the analyser PrimacsSC produced by Skalar; the content of organic carbon (TOC) was calculated from the difference  $TOC = TC - IC$ ,
- total nitrogen (TN) with Kjeldahl's method,
- pH in water (the ratio of 1:5 w/v) electrometrically,
- specific conductivity in the paste (the ratio of 1:2 w/v) with the conductometric analysis.

The percentage contribution of organic matter ( $TOC \cdot 1.74$  [66]), calcium carbonate ( $IC \cdot 8.33$ ) and the mineral fraction were calculated in samples (Table 19), which enabled the classification of sediments according to Markowski [55].

The analysed sediment samples collected in *the littoral zone* of **field lakes (PA)** contained from  $53.6 \text{ g} \cdot \text{kg}^{-1}$  (Lake Zbyszewickie) to  $186.4 \text{ g} \cdot \text{kg}^{-1}$  (Lake Strzałkowo) of organic carbon and up to  $82.8 \text{ g} \cdot \text{kg}^{-1}$  of inorganic carbon. Sediments were also characterized by a highly diverse content of total nitrogen, which ranged from 3.8 to  $18.2 \text{ g} \cdot \text{kg}^{-1}$ . The positive correlation was confirmed between the content of organic carbon and total nitrogen ( $r = 0.9407$ , with  $p < 0.05$ ). Heterogeneity in the content of organic carbon and total nitrogen in individual samples is reflected also in the calculated values of the ratio TOC:TN (10.0-16.2). Electrical conductivity of the sediment ranged from 1657 to  $3630 \mu\text{S} \cdot \text{cm}^{-1}$ , and pH of the sediment – from 6.85 to 7.22 (Table 18).

Sediment samples coming from *the littoral zone* of **forest lakes (LA)** contained from  $85.9$  to  $456.0 \text{ g} \cdot \text{kg}^{-1}$  of organic carbon and were basically characterized by its higher content compared with the sediment of this zone in the field lakes (PA). In the sediment of Lakes Szamoty Duże, Pniewo and Hanki, no inorganic carbon compounds were recorded. In the remaining lakes, the content of inorganic carbon ranged from 13.5 to  $44.0 \text{ g} \cdot \text{kg}^{-1}$  (Lake Sumile and Borowe respectively), whereas the content of total nitrogen ranged from 4.2 to  $29.1 \text{ g} \cdot \text{kg}^{-1}$ . The content of organic carbon was positively correlated with the total nitrogen content ( $r = 0.9815$ , with  $p < 0.05$ ). The value of the ratio TOC:TN for the described sediment samples ranged from 13.5 to 20.5. Sediment samples were highly heterogeneous in respect of salinity and reaction. Electrical conductivity of sediment samples ranged from 873 to  $2800 \mu\text{S} \cdot \text{cm}^{-1}$ , whereas pH – from 4.60 to 7.06 (Table 18).

*Profundal* sediments of **field lakes (PB)** contained from 65.2 to  $220.4 \text{ g} \cdot \text{kg}^{-1}$  of organic carbon and  $7.1$ - $90.1 \text{ g} \cdot \text{kg}^{-1}$  of inorganic carbon. The content of nitrogen was within the range of  $6.2$ - $18.8 \text{ g} \cdot \text{kg}^{-1}$ . The content of total nitrogen was positively correlated with the content of organic carbon ( $r = 0.9890$ , with  $p < 0.05$ ). Compared with littoral sediment, most of the profundal sediment samples contained more organic carbon, inorganic carbon and nitrogen. Values of the TOC:TN ratio ranged from 10.6 to 13.0 and for most of the samples these values were lower compared with littoral samples. Sediments were characterized by pH values within the range of 6.93-7.30 and conductivity – from 1862 to  $3130 \mu\text{S} \cdot \text{cm}^{-1}$  (Table 18).

Table 18. Physicochemical properties of lakes bottom sediments [14]

Lake name	Sample symbol	TOC	IC (g·kg <sup>-1</sup> )	TN	TOC:N <sub>t</sub>	pHH <sub>2</sub> O	χ (μS·cm <sup>-1</sup> )
Bobrów	PA42	112.4	0.0	8.6	13.1	6.89	1657
Murwinek	PA22	181.9	37.1	18.2	10.0	7.15	3630
Zbyszewickie	PA25	53.6	10.2	3.8	14.0	7.13	1872
Pawłowskie	PA15	125.5	46.5	11.1	11.3	6.93	2290
Czeszewskie	PA60	75.6	82.8	4.7	16.2	7.22	2110
Strzałkowo	PA27	186.4	15.2	13.6	13.7	6.94	2280
Żońskie	PA17	83.3	39.3	8.2	10.2	6.85	2080
Czworokątne	LA8	227.6	42.6	16.5	13.8	6.76	2800
Krapsko Małe	LA46	85.9	13.5	4.2	20.5	7.06	1431
Sumile	LA35	145.2	19.2	10.8	13.5	6.85	2060
Hanki	LA29	201.9	0.0	11.3	17.8	6.54	1885
Borowe	LA33	213.8	44.0	15.5	13.8	6.92	2190
Szamoty Duże	LA11	456.0	0.0	29.1	15.7	5.65	873
Pniewo	LA54	188.0	0.0	12.0	15.7	4.60	1480
Bobrów	PB44	127.6	7.1	11.2	11.4	6.98	1887
Murwinek	PB23	220.4	30.6	18.8	11.8	6.96	3130
Zbyszewickie	PB26	135.9	55.8	11.1	12.2	7.30	1862
Pawłowskie	PB16	134.8	52.3	11.1	12.2	6.93	2190
Czeszewskie	PB61	65.2	90.1	6.2	10.6	7.30	2300
Strzałkowo	PB28	199.8	25.6	15.4	13.0	7.20	2600
Żońskie	PB18	100.8	57.0	9.5	10.6	7.08	2050
Czworokątne	LB9	380.0	4.3	19.0	20.0	6.69	2220
Krapsko Małe	LB47	85.3	61.9	6.9	12.4	7.45	1787
Sumile	LB36	89.9	27.7	7.4	12.1	7.06	1631
Hanki	LB30	339.4	0.0	23.9	14.2	6.45	1771
Borowe	LB34	356.4	7.8	20.9	17.0	6.74	2690
Szamoty Duże	LB12	300.0	0.0	19.6	15.3	4.77	2050
Pniewo	LB55	184.6	0.0	14.1	13.1	4.43	1712

PA – the symbol of sediment samples collected from the littoral zone of field lakes

LA – the symbol of sediment samples collected from the littoral zone of forest lakes

PB – the symbol of sediment samples collected from the profundal zone of field lakes

LB – the symbol of sediment samples collected from the profundal zone of forest lakes

*Profundal* sediment samples of **forest lakes (LB)** contained from 85.3 to 380.0 g·kg<sup>-1</sup> of organic carbon and to 61.9 g·kg<sup>-1</sup> of inorganic carbon. The total nitrogen content was diverse and amounted to 6.9-23.9 g·kg<sup>-1</sup>; the determined content was usually higher compared with littoral sediment samples. The content of organic carbon was correlated with total nitrogen ( $r = 0.9464$ , with  $p < 0.05$ ). Values of the TOC:TN ratio ranged from 12.1 to 20.0. Electrical conductivity of the described sediment samples ranged from 1631 to 2690 μS·cm<sup>-1</sup>, whereas pH – from 4.43 to 7.45 (Table 18) [14, 15, 16, 18].

Bottom sediments collected in the littoral and profundal zones of lakes situated in catchment areas with agricultural or forest land use development were characterized by heterogeneous content of both organic (TOC) and inorganic carbon. The content of TOC fluctuated within very broad limits from 53.6 to 456 g·kg<sup>-1</sup>, whereas the content of inorganic carbon ranged from 0.0 to 90.1 g·kg<sup>-1</sup>. Also concentrations of total nitrogen

were very different from each other (3.8-29.1 g·kg<sup>-1</sup>). Diversification of the organic carbon and total nitrogen content was reflected in values of the calculated ratio TOC:TN. The values varied and were relatively high. These high values indicate a considerable contribution of vascular plants' remains in the organic matter of littoral and profundal sediments in lakes of both types. Based on the performed analysis of clusters, three main groups of sediment samples were distinguished, which comprised both samples from forest and field lakes (Fig. 22). The differences in sediment properties were not significant enough to use them for an explicit division.

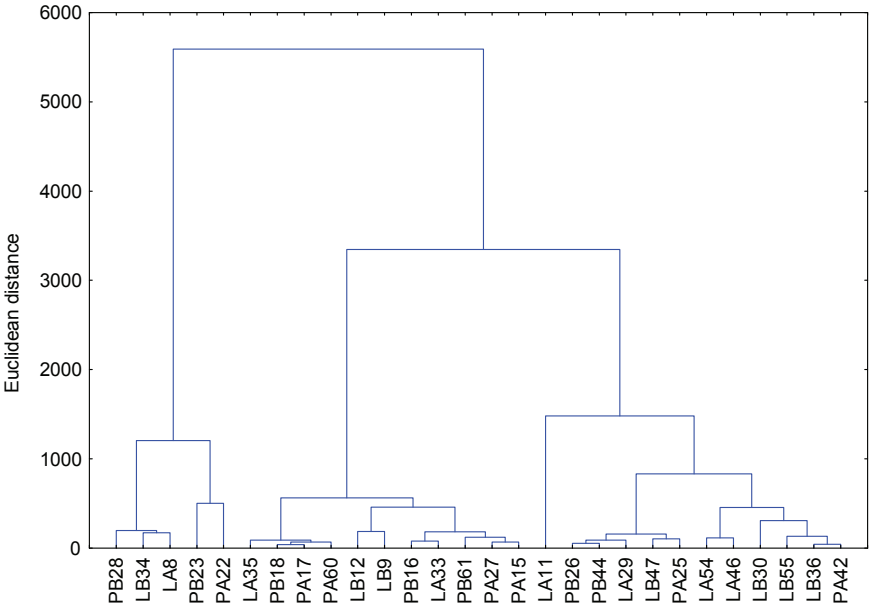


Fig. 22. Grouping of all bottom sediment samples based on physicochemical characteristics (TOC, IC, TN, TOC:TN, pH, electrical conductivity) [14]

The analysis of clusters performed for sediment samples from field lakes (Fig. 23) revealed that physicochemical properties of littoral and profundal sediment samples were similar. Also properties of sediments in forest lakes did not depend on the location of sampling (Fig. 24). Based on the performed statistical analysis, one can conclude that contrary to lake waters, characteristics of bottom sediments are determined to a lesser extent by the catchment area management, and they do not show major differences regarding sampling location. Perhaps this is caused by a relatively small area and depth of water reservoirs, which results in the lack of diversity in the material deposited in different parts of a lake.

Based on the performed classification, one can conclude that the described sediments represent all three types of bottom sediments, however the carbonate sediments occurred in the largest quantities (14), and they occurred mainly in lakes within agricultural catchment areas (Table 19).

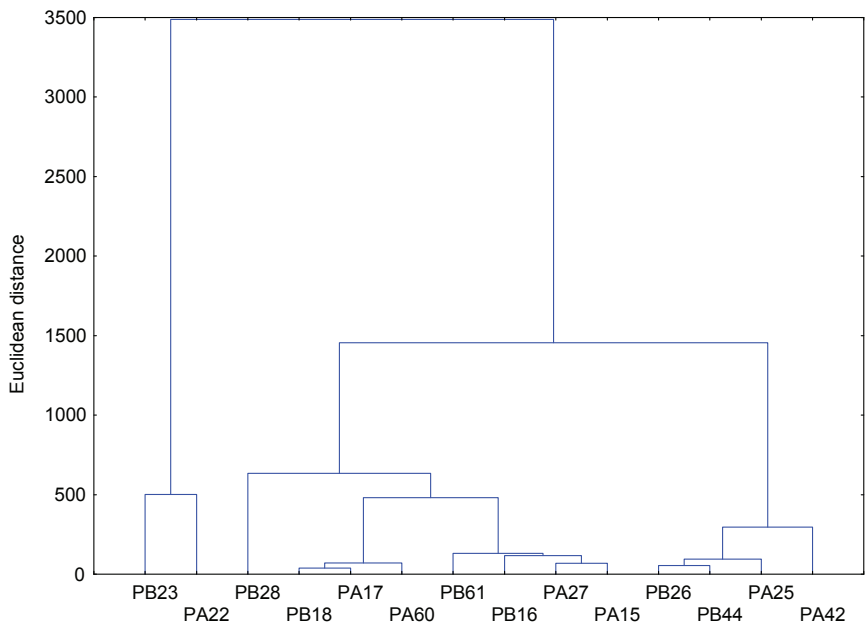


Fig. 23. Grouping of all bottom sediment samples from field lakes based on physicochemical characteristics (TOC, IC, TN, TOC:TN, pH, electrical conductivity) [14]

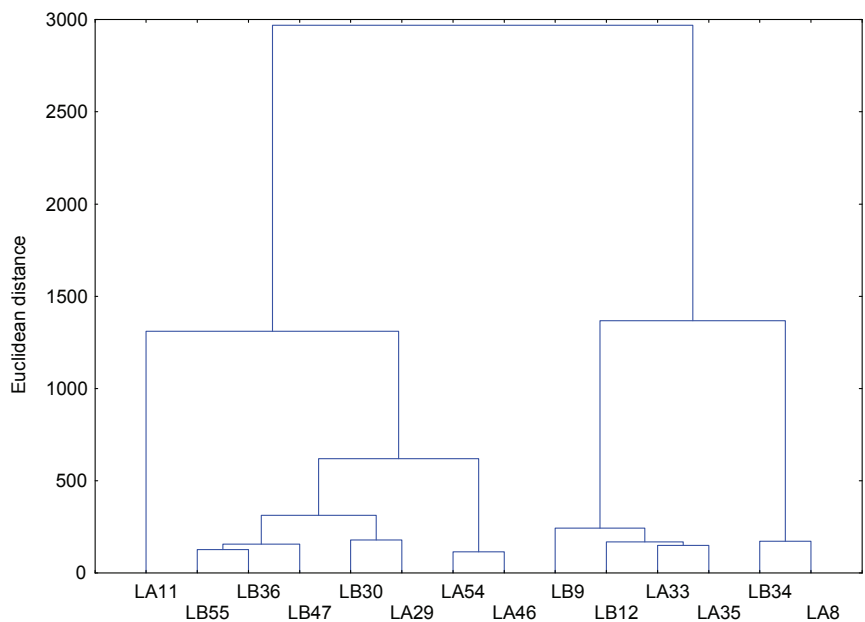


Fig. 24. Grouping of all bottom sediment samples from forest lakes based on physicochemical characteristics (TOC, IC, TN, TOC:TN, pH, electrical conductivity) [14]



Table 19. The composition of bottom sediments in lakes (weight %) [14]

Lake name	Sample symbol	Organic matter	Calcium carbonate	Mineral fraction	Type of gyttja
Bobrów	PA42	19.6	0.0	80.4	clayey
Murwinek	PA22	31.7	30.9	37.4	detrital-calcareous
Zbyszewickie	PA25	9.3	8.5	82.2	clayey
Pawłowskie	PA15	21.8	38.8	39.4	clayey-calcareous
Czeszewskie	PA60	13.2	69.0	17.8	calcareous
Strzałkowo	PA27	32.4	12.7	54.9	clayey
Żońskie	PA17	14.5	32.8	52.7	clayey-calcareous
Czworokątne	LA8	39.6	35.5	24.9	detrital-calcareous
Krapsko Małe	LA46	15.0	11.3	73.7	clayey
Sumile	LA35	25.3	16.0	58.7	clayey
Hanki	LA29	35.1	0.0	64.9	sandy-clayey
Borowe	LA33	37.2	36.7	26.1	detrital-calcareous
Szamoty Duże	LA11	79.3	0.0	20.7	coarse detritus
Pniewo	LA54	32.7	0.0	67.3	sandy-clayey
Bobrów	PB44	22.2	5.9	71.9	clayey
Murwinek	PB23	38.4	25.5	36.1	detrital-calcareous
Zbyszewickie	PB26	23.7	46.5	29.8	clayey-calcareous
Pawłowskie	PB16	23.5	43.6	32.9	clayey-calcareous
Czeszewskie	PB61	11.3	75.1	13.6	calcareous
Strzałkowo	PB28	33.0	21.3	45.7	(detrital-calcareous)
Żońskie	PB18	17.5	47.5	35.0	clayey-calcareous
Czworokątne	LB9	66.1	3.6	30.3	coarse detritus
Krapsko Małe	LB47	14.8	51.6	33.6	calcareous
Sumile	LB36	15.6	23.1	61.3	(clayey-calcareous)
Hanki	LB30	59.1	0.0	40.9	fine detritus
Borowe	LB34	62.0	6.5	31.5	coarse detritus
Szamoty Duże	LB12	52.2	0.0	48.8	fine detritus
Pniewo	LB55	32.1	0.0	67.9	sandy-clayey

### 3.6. SOURCES AND PROPERTIES OF HUMIC SUBSTANCES IN BOTTOM SEDIMENTS OF LAKES

The content of humic substances in organic matter ranges from 60 to 70% in young sediments of lakes, to more than 90% in older sediments [39]. Although humic substances are difficult to characterize, they provide relevant information on sources and transformations of the accumulated organic matter. Generally humic substances are divided into fulvic acids (soluble in acids and bases), humic acids (soluble in bases) and humins (insoluble in acids and bases).

Many theories explaining the origin of humic substances have been presented, but due to a variety of precursors and accumulation environments, none of them is universal. Four main theories related to formation of soil humic substances were summarised by Stevenson [81]: (a) progressing degradation of lignin by microorganisms to humic and then fulvic acids, (b) progressing degradation of lignin by microorganisms to fulvic and then humic acids, (c) degradation of lignin to phenol monomers, from which

humic substances are produced, (d) condensation of carbohydrates and amino acids to humic substances.

Organic matter of aquatic environments usually contains less lignin and cellulose, i.e. potential precursors of humic substances, compared with organic matter of terrestrial environments. Thurman [85] presented hypotheses concerning the formation of humic substances in the absence of lignin material. Soil washing in the catchment area, leaching of aquatic plants' tissues, photooxidation of organic matter dissolved in the surface waters, and the lysis of algae cells are a likely source of compounds with low molecular weight, which later polymerize to humic substances.

Elemental composition is one of the main characteristics describing the humic substances. Table 20 presents the mean content values of the main chemical elements in humic and fulvic acids, as well as in humins.

Table 20. Elemental composition of humic substances contained in bottom sediments of the lakes [39]

Number of samples	Humic acids (22)	Fulvic acids (5)	Humins (2)
Component (weight %)			
carbon	52.05 ± 3.61*	44.98 ± 3.90	53.82 ± 4.50
hydrogen	5.67 ± 0.65	5.12 ± 1.24	4.88 ± 1.00
nitrogen	5.63 ± 1.08	7.63 ± 0.56	4.17 ± 0.68
oxygen	36.55 ± 4.27	42.27 ± 4.69	36.78 ± 4.62
Atomic ratios			
H:C	1.30 ± 0.13	1.34 ± 0.24	1.08 ± 0.13
N:C	0.093 ± 0.018	0.147 ± 0.020	0.068 ± 0.016
O:C	0.533 ± 0.094	0.716 ± 0.146	0.518 ± 0.108

\* standard deviation

Humic acids compared with fulvic acids contain more carbon and less nitrogen. Humins, compared with humic acids, contain more carbon and much less nitrogen.

The comparison of qualitative parameters of humic acids from different environments (soils, marine and lacustrine sediment) indicates close interrelations between humic acids of lacustrine bottom sediments with primary material (e.g. phytoplankton), and a relatively low degree of humification [37]:

the content of carbon (wt %): soil (57.94) > sea (52.31) ~ lake (52.05)  
 atomic ratio H:C: sea (1.42) > lake (1.30) > soil (0.98)  
 atomic ratio N:C: lake (0.093) > sea (0.058) ~ soil (0.055)

In UV-VIS spectra for materials of plant origin, the presence of a band within the range of 275-280 nm was determined. In the literature [47, 51, 71], it is assumed that absorption within this range is characteristic of aromatic structures of lignin origin. Relatively high values of absorbance at the wavelength of 600 nm of certain HAs in bottom sediments is explained by the inflow of humic acids from the catchment soils [37]. Ishiwatari observed the presence of an additional band within the range of ca. 410 nm. The presence of this band was associated with the occurrence of pigment coming from chlorophyll [38, 94]. Similar results were obtained by Povoledo and co-authors [69]. However, one more band has been observed at ca. 670 nm. It is assumed that bands 410 and 670 nm are associated with the presence of pheophytin a. One of the

main criteria characterizing the humic substances from different types of soils is the value of absorbance of their solutions at the wavelength of 465 nm and the value of the ratio  $A_{4/6}$  (the absorbance ratio at 465 and 665 nm). Chen and co-authors [12] proved that the value of this ratio depends on the average molecular weight, the content of carboxylic acid groups and the percentage content of carbon and oxygen in humic substances.

### 3.7. CHARACTERISTICS OF HUMIC ACIDS FROM BOTTOM SEDIMENTS OF LAKES

Elemental composition is thought to be one of the basic characteristics of humic substances, which can be used in their identification and inference about their structure. The results of the elemental composition analysis are presented in Table 21.

Table 21. Elemental composition of humic acids from lacustrine bottom sediments (mean values, in atomic %) [14, 15]

Samples	C	H	N	O
From littoral	32.49	47.06	2.86	17.60
From profundal	31.73	48.29	2.97	17.00
LSD with $p < 0.05$	0.536	0.778	ns	ns
From field lakes	31.40	48.86	3.05	16.68
From forest lakes	32.81	46.48	2.79	17.91
LSD with $p < 0.05$	0.536	0.778	0.209	0.702

ns – non-significant differences

Humic acids isolated from the *littoral* bottom sediments of **lakes with the agricultural land use in the catchment area (PA)** contained on average 31.66% of carbon and 48.48% of hydrogen. The average nitrogen and oxygen content was 3.06% and 16.81%, respectively. No significant correlation between the content of chemical elements was found for humic acids.

The elemental composition of humic acids obtained from the *littoral* bottom sediments of **lakes with the forest catchment area (LA)** was different. The content of carbon and hydrogen was on average 32.32% and 45.64%, respectively. Significant negative correlation between the content of carbon and hydrogen was confirmed (the correlation coefficient  $r = -0.9395$  at  $p < 0.05$ ). The content of nitrogen on average amounted to 2.66% and was correlated with the content of carbon ( $r = -0.8176$ ,  $p < 0.05$ ) and hydrogen ( $r = 0.8568$ ,  $p < 0.05$ ). The percentage content of oxygen in the described HA reparations was on average 18.39%.

The oxygen content was positively correlated with the carbon content ( $r = 0.8686$ ,  $p < 0.05$ ) and negatively with the content of hydrogen ( $r = -0.9783$ ,  $p < 0.05$ ) and nitrogen ( $r = -0.9075$ ,  $p < 0.05$ ). Compared with HAs isolated from the littoral sediments of field lakes, the humic acids were characterized by a higher content of carbon and oxygen and a lower content of hydrogen and nitrogen.

Humic acids isolated from *profundal* bottom sediments of **field lakes (PB)** were characterized by a relatively low content of carbon – on average 31.15% and a high content of hydrogen – on average 49.25%. The average content of nitrogen and oxygen amounted to 3.05% and 16.55%, respectively.

Compared with HAs from profundal sediments of field lakes, humic acids obtained from *profundal* sediments of **forest lakes (LB)** were characterized by a higher percentage content of carbon (on average 32.31%) and oxygen (on average 17.44%), and a smaller content of hydrogen (on average 47.33%) and nitrogen (on average 2.92%). For the analysed HA preparations, a significant negative correlation was determined between the content of carbon and hydrogen (the correlation coefficient  $r = -0.7615$  with  $p < 0.05$ ).

The percentage content of particular chemical elements is reflected also in the calculated values of atomic ratios and the degree of internal oxidation, which are presented in Table 22 [14, 15].

Table 22. Mean values of atomic ratios and the degree of internal oxidation for humic acids ( $\omega$ ) from bottom sediments of the lakes [14, 15]

Samples	H:C	N:C	O:C	O:H	$\omega$
From littoral	1.46	0.088	0.54	0.38	-0.104
From profundal	1.52	0.094	0.54	0.35	-0.169
LSD with $p < 0.05$	0.044	ns	ns	0.022	0.049
From field lakes	1.56	0.097	0.53	0.34	-0.202
From forest lakes	1.42	0.085	0.55	0.39	-0.071
LSD with $p < 0.05$	0.044	0.007	ns	0.022	0.049

ns – non-significant differences

The mean value of the H:C ratio for humic acids from *littoral* sediments of **field lakes** was 1.54, and the N:C ratio – 0.097. Mean values of the ratios O:C and O:H were 0.53 and 0.35, respectively. For all HA samples, the degree of internal oxidation had negative values.

For humic acids from *littoral* sediments of **forest lakes**, the H:C ratio on average amounted to 1.37, and the N:C ratio – 0.080. These values were lower compared with those obtained for HA preparations from littoral sediments of field lakes. Large dispersion in values of O:C and O:H ratios reflected differences in the elemental composition of humic acids from sediments of forest lakes. There were also major differences in the value of internal oxidation state – it had a positive value for two samples, and a negative value for the remaining ones, which affected a relatively high mean value of internal oxidation.

Values of H:C and N:C ratios for preparations of humic acids from *profundal* sediments coming from lakes of both types had values similar to those obtained for HAs of *littoral* sediments. Values of the O:C ratio were similar for all HA samples, and values of the O:H ratio were higher for humic acids from *profundal* sediments of **forest lakes**. Values of internal oxidation for all samples from both types of lakes were negative, and HAs isolated from sediments of **field lakes** had lower values.

When comparing the elemental composition of humic acids from lakes of both types, one can conclude that humic acids from bottom sediments of forest lakes are characterized by a higher content of carbon and oxygen, and a lower content of hydrogen and nitrogen compared with HAs from field lakes (Table 21).

Values of the H:C ratio indicate a more aromatic nature of humic acids from sediments of forest lakes. A positive value of internal oxidation was obtained for two samples of humic acids from littoral sediments of forest lakes (Table 22). HAs of soil are characterized by a positive value of internal oxidation [19, 29]; in the case of bottom

sediments from water reservoirs, a positive value of this parameter was recorded for humic acids of bottom sediments from the Bay of Szczecin, which were affected by the runoff from peat soils [17].

Spectrometric properties of humates within the range of UV-VIS are presented in Tables 23 and 24. It is assumed that the value of  $A_{280}$  defines the content of lignin-type compounds, the value of  $A_{465}$  is determined by the content of substances in the initial stage of decomposition, and  $A_{665}$  reflects the content of substances characterized by a high degree of humification. It was found that higher absorbance values at 280 and 465 nm were characteristic of humate solutions from bottom sediments of **forest lakes** (Table 23). For both types of lakes, the absorbance values at 280 and 465 nm were higher for humates from *littoral* sediments compared with values obtained for humates of *profundal* sediments. The highest values of absorbance at 665 nm were recorded for humate solutions from *profundal* sediments of **field lakes**.

Table 23. Mean values of absorbance for humates from bottom sediments of the lakes [14, 15]

Samples	Wavelength (nm)				
	280	400	465	600	665
From littoral	0.467	0.164	0.0751	0.0238	0.0160
From profundal	0.401	0.154	0.0687	0.0229	0.0171
LSD with $p < 0.05$	0.061	ns	ns	ns	ns
From field lakes	0.365	0.144	0.0604	0.0203	0.0168
From forest lakes	0.503	0.173	0.0833	0.0263	0.0164
LSD with $p < 0.05$	0.061	0.026	0.0142	0.0046	n.s.

ns – non-significant differences

Table 24. Mean values of the absorbance ratios,  $\Delta\log K$  and values of four derivatives for humates from bottom sediments of the lakes [14, 15]

Samples	$A_{2/4}$	$A_{2/6}$	$A_{4/6}$	$\Delta\log K$	$D_{404}^4$	$D_{657-660}^4$
From littoral	6.34	29.42	4.66	0.858	10.83	1.85
From profundal	5.89	24.23	4.09	0.830	15.66	2.91
LSD with $p < 0.05$	0.439	3.448	0.423	ns	3.44	0.615
From field lakes	6.09	22.06	3.61	0.853	17.83	3.39
From forest lakes	6.13	31.59	5.14	0.834	8.66	1.36
LSD with $p < 0.05$	ns	3.448	0.423	ns	3.44	0.615

ns – non-significant differences

The highest values of the  $A_{2/4}$  ratio were obtained for humates from *littoral* sediments of **field lakes** – on average 6.40. Values of the  $A_{2/6}$  ratio, describing the content of lignin-type compounds resistant to degradation in relation to strongly humified organic matter, were the highest for humates from *littoral* sediments of **forest lakes** (on average 34.59). Compared with other samples, these samples were also characterized by higher values of the ratio  $A_{4/6}$  – the range of 4.80-6.71 (on average 5.52). When comparing the obtained results, one can conclude that values of the absorbance ratios  $A_{2/4}$ ,  $A_{2/6}$  and  $A_{4/6}$  were significantly higher for humates coming from *littoral* sediments, and values of the absorbance ratios  $A_{2/6}$  and  $A_{4/6}$  were higher for humates coming from bottom sediments of **forest lakes**. Values of the ratio  $A_{4/6}$  for humic acids from *profundal* sediments of **field lakes** correlated negatively with the hydrogen

content –  $r = -0.7812$ , with  $p < 0.05$ . The parameter  $\Delta\log K$  did not differentiate the samples of humic acids according to their origin or sampling location (Table 24).

Spectra of humic acids were characterized by the presence of a band at 280 nm and in some cases two additional bands at 404 nm and 657-660 nm (Fig. 25), which probably are correlated with the presence of chlorophyll derivatives [38, 69]. Spectra for humates obtained from humic acids extracted from bottom sediments of field lakes were characterized by a higher intensity of additional bands (404 nm, 657-660 nm) compared with humates of “forest lakes”, which is evidenced by calculated values of the fourth derivative for standard spectra (Table 24).

In addition, values of the fourth derivatives  $D4_{404}$  and  $D4_{657-660}$  were higher for humic acids of profundal sediments than for littoral sediments, irrespective of the land use in the drainage basins of the lakes. Values of  $D4_{404}$  below 15 (on average ca. 8) are characteristic of humic acids from bottom sediments of forest lakes; values above 15 (on average ca. 18) are characteristic of HAs from sediments of field lakes.  $D4_{657-660} \cong 2$  is a limit value for humic acids of littoral and profundal sediments. Obviously a detailed explanation of the increased absorption of HA solutions at the wavelength of 404 and ca. 660 nm requires isolation of pigments and an analysis of their structure. For a few samples of HAs, values of the fourth derivative were different from the accepted rules. One can assume, however, that the analysis of seemingly monotonic spectra of humic substances should bring positive effects for their description, and should be a valuable complement to other structural analyses. The subtle analysis of UV-VIS spectra, and particularly their fourth derivatives, made by Miklewska [64], provided grounds for the determination of absorbance ratios for humic acids of soil origin.

Due to the presence of 404 nm band, particularly intensive for samples of humic acids obtained from bottom sediments of field lakes, the parameter  $\Delta\log K$  basically did not differentiate the samples of humic acids according to their origin or sampling location (Table 24). In the case of “field” samples, the presence of the second additional band – 657-660 nm causes the occurrence of relatively high values of  $A_{665}$  absorbance, and at the same time a considerable reduction of the values of  $A_{2/6}$  and  $A_{4/6}$  ratios.

Taking into account the results of the analyses performed on humic acids and the results of their statistical analysis, it can be concluded that the land-use type applied in the drainage basins of the lakes defines the properties of humic acids in bottom sediments. This is evidenced by significant differences between several chemical and physicochemical parameters of humic acids from bottom sediments of different lakes. It seems, however, that despite the documented, statistically significant differences, it is difficult to determine the limit values for parameters of humic acids useful for the supplementary classification of lakes based on the land use prevailing in catchment areas. This is certainly due to high diversity, both in the catchment areas of the lakes and aquatic ecosystems. Among the studied lakes, basically none of catchment areas was homogeneous, i.e. in 100% afforested or agricultural. Therefore, it would more accurate to use the terms: a catchment area with the prevailing forest land use or a catchment area with the prevailing agricultural land use. Bottom sediments of the lakes may also be affected by ecotone zones of different types, such as zones of meadows or woodlots [95]. There is no doubt that humic acids from bottom sediments of littoral zones of field and forest lakes are most different from each other [15]. Smaller differences are between properties of humic acids from profundal sediments. This is caused by the inflow of allochthonous organic matter into water reservoirs and its deposition mainly in the littoral zone [80]. Humic substances deposited in the

profundal zone are mostly of autochthonous origin, which largely eliminates the impact of the catchment area.

Since there are no literature data available, it is difficult to make any references. At the same time, it is difficult to determine if the results and conclusions included in this study are going to be generally applicable. The progress in the research on humic substances will certainly settle the existing doubts and define the directions of further researches.

The conducted research revealed that one should not uncritically interpolate all the research methods applied to soil humic acids (and the analysis of the results obtained by these methods) into investigations of humic acids from bottom sediments [14, 15].

Methodological details of the research which were discussed in the present chapter are presented in the papers by Żdanow [97], Kumada [50], Cieslewicz and Gonet [15] and Cieslewicz [14].

Fig. 25. The comparison of UV-VIS spectra of humates from littoral PA25, LA11 (A) and profundal PB26, LB12 (B) sediments of the field lakes (red line) and the forest lakes (blue line) [14]



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# CHEMIZM WÓD I OSADÓW DENNYCH JEZIOR O ZRÓŻNICOWANYM ZAGOSPODAROWANIU ZLEWNI

## STRESZCZENIE

W pracy zaprezentowano wyniki badań obejmujących 14 jezior zlokalizowanych na terenie województw Wielkopolskiego i Zachodniopomorskiego. Jeziora charakteryzowały się przede wszystkim zróżnicowanym zagospodarowaniem zlewni bezpośredniej. W zlewniach jezior Bobrów, Murwinek, Strzałkowo, Zbyszewickie, Pawłowskie, Żońskie i Czeszewskie przeważały grunty użytkowane rolniczo, natomiast drugą grupę stanowiły jeziora o dominującym udziale lasów w zlewniach – Borowe, Hanki, Sumile, Czworokątne, Szamoty Duże, Krąpsko Małe oraz Pniewo. Badania obejmowały charakterystykę zbiorowisk roślinnych występujących w strefie bezpośrednio otaczającej jeziora, wód jeziornych oraz osadów dennych z uwzględnieniem właściwości substancji humusowych.

Zbiorowiska roślinne zostały scharakteryzowane na podstawie zdjęć fitosocjologicznych wykonane metodą Brauna-Blanqueta. Próbkę wód jeziornych pobrano do analiz w okresie cyrkulacji wiosennej (warstwa powierzchniowa) oraz w czasie stagnacji letniej (warstwa powierzchniowa i naddenna). W próbkach wód oznaczono metodami standardowymi pH, przewodność właściwą, zawartość Fe, Ca, Mg,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , azotu metodą Kjeldahla,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  oraz  $\text{HCO}_3^-$ . Próbkę osadów dennych pobrano z litoralu oraz profundalu i oznaczono w nich zawartość całkowitego węgla organicznego (TOC), azotu ogółem (TN), węgla nieorganicznego (IC), pH oraz przewodność właściwą. Z próbek osadów dennych wyekstrahowano kwasy huminowe (KH) i oznaczono ich skład pierwiastkowy oraz właściwości spektrometryczne w zakresie UV-VIS.

Na podstawie przeprowadzonych badań stwierdzono, że wody jezior o polnym charakterze zlewni w okresie cyrkulacji wiosennej charakteryzowały się istotnie wyższą przewodnością właściwą oraz wyższą zawartością ortofosforanów(V), azotanów(V), chlorków wapnia i magnezu w porównaniu z wodami jezior o leśnym charakterze zlewni. Także w okresie stagnacji letniej wody warstwy powierzchniowej, jak i naddennej jezior polnych cechowały się wyższą przewodnością właściwą i wyższą zawartością chlorków, wapnia i magnezu niż wody jezior śródlęśnych. Osady dennie jezior obu typów odznaczały się silnie zróżnicowaną zawartością TOC, IC oraz TN. Zróżnicowanie materiału organicznego wchodzącego w skład osadów dennych odzwierciedlają obliczone wartości stosunku TOC:TN. Generalnie wyższe wartości tego stosunku stwierdzone dla osadów z jezior śródlęśnych wskazują na znaczny udział materiału pochodzenia lądowego w puli materii organicznej osadów jezior tego typu.

Kwasy huminowe wyekstrahowane z osadów dennych o polnym charakterze zlewni charakteryzowały się niższą zawartością węgla i tlenu oraz wyższą zawartością wodoru i azotu w porównaniu z kwasami wyekstrahowanymi z osadów dennych jezior śródlęśnych. Zróżnicowanie składu pierwiastkowego znalazło swoje odzwierciedlenie w wartościach obliczonych stosunków atomowych oraz wartościach stopnia utlenienia wewnętrznego. Wyższymi wartościami stosunków H:C i N:C oraz niższym stopniem utlenienia wewnętrznego w porównaniu z kwasami huminowymi z osadów jezior



śródleśnych charakteryzowały się KH z jezior śródpolnych. Wyższymi wartościami absorbancji przy długościach fal 280, 400, 465, 600 nm odznaczały się alkaliczne roztwory kwasów huminowych wyekstrahowanych z osadów jezior śródleśnych. W widmach otrzymanych dla kwasów huminowych z jezior śródpolnych stwierdzono występowanie dwóch intensywnych pasm absorpcji przy długościach fal 404 i około 660 nm. Jest to związane z obecnością fragmentów pochodzenia barwnikowego w strukturze kwasów huminowych. Pasma te charakteryzowały się znacznie mniejszą intensywnością w widmach kwasów huminowych wyekstrahowanych z osadów jezior śródleśnych.

Biorąc pod uwagę wyniki wykonanych analiz kwasów huminowych i ich analizy statystycznej można stwierdzić, że sposób użytkowania zlewni jezior determinuje właściwości kwasów huminowych osadów dennych. Nie ulega wątpliwości, że najbardziej różnią się od siebie kwasy huminowe osadów dennych strefy litoralowej jezior śródpolnych i śródleśnych. Mniejsze różnice występują między właściwościami kwasów huminowych osadów profundalowych. Jest to spowodowane dopływem do zbiorników allochtonicznej materii organicznej i deponowaniem jej głównie w strefie litoralu. Substancje humusowe deponowane w strefie profundalu są pochodzenia głównie autochtonicznego, co niweluje w dużym stopniu wpływ zlewni.