# CARBON AND OXYGEN ISOTOPE COMPOSITION OF ORGANIC MATTER AND CARBONATES IN RECENT LACUSTRINE SEDIMENTS

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Key words: STABLE CARBON and OXYGEN ISOTOPES, RADIOCARBON, LAKE ENVIRONMENT **Abstract:** The distribution of stable isotopes (<sup>18</sup>O and <sup>13</sup>C) and radiocarbon in organic materials, carbonates and water samples collected from the environment of lacustrine sediments in Gosciąż Lake (Central Poland) and Wigry Lake (NE Poland) were investigated. The oxygen and carbon isotopic analysis of terrestrial semi submerged and submerged plants, shells and water samples were compared with the results of the uppermost sediments from lakes. It was found that the concentration of isotopes in different components of organic and carbonate materials in lakes and their environments are reflected in isotope composition averaging of lakes sediments, whereas the isotope composition of plants and carbonate depends on biogeochemical factors.

The research carried out revealed significant variations in the distribution of the stable isotopes and <sup>14</sup>C in different elements of lacustrine ecosystem. We have analyzed mean values and variations of <sup>14</sup>C concentration,  $\delta^{18}$ O,  $\delta^{13}$ C of plants, carbonates and the relationship between the total content of carbon and  $\delta^{13}$ C. In the case of plants, the isotope composition depends also on the physiognomy and the photosynthesis pathway. We noticed variations in  $\delta^{13}$ C and  $\delta^{18}$ O within plant tissues, variations in  $\delta^{13}$ C among whole tissue material and alphacellulose, carbon isotopic composition of photosynthetically fixed carbon and syntaxonomic dependences and then we compared the results of isotope composition of plants and carbonates in Wigry Lake and Gościąż Lake.

#### 1. INTRODUCTION

Investigations performed in Gliwice Radiocarbon Laboratory concern radiocarbon dating of lake sediments from depth wells, dating of the youngest sediments by <sup>14</sup>C, <sup>137</sup>Cs and <sup>210</sup>Pb methods and measurements of stable isotopes (<sup>13</sup>C and <sup>18</sup>O) in carbonates. The goal of dating is the construction of an absolute time scale of past climatic changes. The climatic changes were investigated by studying isotope composition of carbon and oxygen of sediments, diatoms and by analyzing variations of pollen density in sediment cores. To solve a problem of systematic error connected with radiocarbon reservoir effect and apparent age, the following approach was adopted: (1) carbon isotopic composition was analyzed in contemporary plants and in carbonates in sediments, (2) the radiocarbon reservoir effect in both materials was estimated.

The aim of these investigations was to characterize carbon and oxygen composition of organic matter and carbonates in recent sediments of Wigry Lake and Gościąż Lake. As a result of the studies we have received the information about carbon and oxygen cycle in the Wigry Lake and Gościąż Lake environments.

Stable isotopes are a useful tool in investigations of plant physiology, ecology and also in the study of lake's ecosystem and its dynamics. The isotopic fractionation occurs during basic physiological processes responsible for plant growth. It is well known that stable carbon ( $\delta^{13}C$ ) and oxygen ( $\delta^{18}O$ ) isotope ratios of plants are determined by ambient climatic parameters such as temperature,

humidity, precipitation and the physiology of the plant. The isotopic response of the plants to changing ambient climate is also known to be site-specific and species dependent in many cases (Aucour *et al.*, 1996; Forquhar and Lloyd, 1993; Rajagopalan *et al.*, 1999; Yakir *et al.*, 1994).

The isotope fractionation effects are important for the study of metabolic fluxes in plants and other problems in plants physiology (Schmidt and Gleixner, 1998).

$$\delta_{\text{sample}} = \frac{R_{\text{samp}} - R_{\text{stand}}}{R_{\text{stand}}} \cdot 1000 \,\%$$
(1.1)

where R represents the ratio of the heavy to the light isotope. The reference standard for carbon is the isotopic ratio in the Vienna Peedee Belemnite (VPDB) and for oxygen is the isotopic ratio in the Vienna Standard Mean Ocean Water (VSMOW) and Vienna Peedee Belemnite (VPDB) (McCarroll and Loader, 2004).

#### Carbon isotopes in plants

The  $\delta^{13}$ C content of the plant material is correlated with the type of photosynthetic cycle followed by the organism.  $\delta^{13}$ C values for C<sub>3</sub> plants fall around -26% and for  $C_4$  plants around -13%, while those of CAM plants cover the whole range of  $C_3$  and  $C_4$  plants. There are small  $\delta^{13}$ C differences between various plant components: leaves appear to be slightly depleted in <sup>13</sup>C with respect to the total plant. Certain  $\delta^{13}$ C differences exist between various chemical components of plant material: sugar, cellulose and hemi-cellulose show  $\delta^{13}$ C values close to the mean plant carbon isotopic composition, pectin appears to be enriched in <sup>13</sup>C, while lignin and lipids are depleted in this isotope relative to the total plant (Deines, 1980). The process of photosynthesis, as well as a few other processes, such as water temperature, hydrodynamics, and pH level may influence the range and variability of isotopic composition of marine autotrophy and favour the lighter form of carbon and lead to variations in carbon isotope ratios (Deines, 1980; Rajagopalan et al., 1999; Raven et al., 1993).

Interpretation of variability in  $\delta^{13}$ C values between environmental reservoirs requires an understanding of physical and chemical processes which favour one isotope over another. Natural chemical or physical processes introduce fractionation of the carbon isotopes during carbon uptake and alter the <sup>13</sup>C/<sup>12</sup>C and <sup>14</sup>C/<sup>12</sup>C isotopic ratios.

It was observed, that the carbon isotopic fraction of living matter and carbonate showed systematic differences with organic matter being depleted in <sup>13</sup>C (Deines, 1980). The depletion of the <sup>13</sup>C in the plant material compared to the source CO<sub>2</sub> is linked with photosynthesis. The consistent isotopic composition differences exist between certain plant types. Plants were classified on the basis of their carbon isotopic composition in two groups: with low and high  $\delta^{13}$ C values. In a particular growth environment, plants following the C<sub>3</sub> pathway of carbon fixation are depleted in <sup>13</sup>C by 12-14% compared to plants following the C<sub>4</sub> pathway. In comparison to the large range in isotopic composition found for different plants, the variations in the  $\delta^{13}$ C among different parts of the same plant are minor. A trend of increasing <sup>12</sup>C content with the growing season is observed.

The uptake of carbon from the  $CO_2$  reservoir of the atmosphere and surface waters by photosynthesis in the form of complex organic molecules is one of the most important processes affecting changes in the carbon and oxygen isotopic composition in the geochemical cycle (Deines, 1980).

#### **Oxygen** isotopes

The main characteristic of the oxygen cycle is its connection with a part of the carbon cycle that plants have a key position in. Measurements of  $\delta^{18}$ O support the interpretation of differences in carbon isotope discrimination among individuals growing in the same environment. Gonfiantini et al. (1965) were first to demonstrate that the water in leaves is enriched in comparison to that supplied from the soil. The measurements of  $\delta^{18}$ O were focused on wood and aimed at using tree rings as "isotope thermometers". The main issues were the origin of the oxygen atoms and how  $\delta^{18}$ O varied between compounds and between the early and late wood. It was found that the cellulose oxygen was derived from CO<sub>2</sub>, and proved that lignin was less enriched than cellulose; it was also demonstrated that cellulose was enriched compared to the whole wood. The possible evaporative effects in leaves should be taken into account as well. The cellulose of aquatic plants was enriched in  $\delta^{18}$ O compared to the water in which they grew. The  $\delta^{18}$ O of the water in plants determines  $\delta^{18}$ O of cellulose.

Water containing the lighter isotope of oxygen will evaporate more easily than that containing the heavier isotope, hence the source water is isotopically heavier than the moisture that evaporates from it. The effect is temperature dependent, so that cold air masses collect moisture that is isotopically lighter than that which evaporates under warmer conditions. When moisture vapour condenses, the opposite is true, with the heavy isotope condensing more readily, and again the isotopic ratio depends on the temperature at which condensation takes place. Global variations in the  $\delta^{18}$ O of precipitation are thus linked in a complex way to climate (Deines, 1980; Farquhar *et al.*, 1998; McCarroll and Loader, 2004).

#### Radiocarbon

Carbon dioxide in the atmosphere contains a small amount of radioactive <sup>14</sup>C. Through photosynthesis, the radiocarbon is incorporated into the Earth's plant and animal life cycle. The atmospheric CO<sub>2</sub> enters the lake by exchange via its surface and the dissolved inorganic carbon of ground inflow and precipitation are principal sources of <sup>14</sup>C in lakes. The limnological conditions are frequently controlled by the seasonal and secular variations. The proportions of these two ways of input determine the magnitude of the reservoir effect in freshwater lakes. An accurate and reliable <sup>14</sup>C dating of lake sediments requires a study of the temporal changes of the reservoir effect by analysis of organic and carbonate fractions. The most reliable <sup>14</sup>C dates are obtained from terrestrial plant remains (Geyh *et al.*, 1998). The Conventional Radiocarbon Age ( $T_{CONV}$ ; Stuiver and Polach, 1977) and real age (T; Pazdur *et al.*, 1999) for sediments are calculated using the radiocarbon decay equation:

$$A = A_0 e^{-\lambda T} \tag{1.2}$$

$$\lambda = \frac{\ln 2}{T_{CONV1/2}} \tag{1.3}$$

$$T_{CONV} = 8033 \cdot \ln \frac{S_0}{A} \tag{1.4}$$

$$T = 8033 \cdot \ln \frac{A_0}{A} \tag{1.5}$$

where:

 $S_0$  – is the activity (in Bq) of the modern biosphere standard,

A –is the activity (in Bq) of the sample,

 $A_0$  – is the initial radiocarbon activity (in Bq) of the sample.

The ratio of the initial radiocarbon activity in the measured sample divided by activity of the modern biosphere standard is called dilution factor (q).

$$q = \frac{A_0}{S_0} \tag{1.6}$$

Thus, the conventional radiocarbon age  $(T_{CONV})$  for sediments is the sum of the reservoir (or apparent) age  $(T_{R})$  and the real (T) age of the sample:

$$T_{CONV} = -8033 \cdot \ln q + 8033 \cdot \ln \frac{A_0}{A}$$
(1.7)

And the apparent age is defined as:

$$T_R = -8033 \cdot \ln q \tag{1.8}$$

## 2. THE STUDY AREA

Wigry Lake (Fig. 1) is situated on the border which separates two geographical regions - the Eastern Suwałki Lake District and the Augustowska Plain, in the central part of Wigry National Park (54°01'N, 23°01'07"E). It is the largest and the 5th deepest basin in Poland. The main tributary is the Czarna Hańcza River that flows into Lake Wigry from the west and outflows from the east. The Suwałki Lake District is characterized by young glacial landscape formed during the last phase of the Scandinavian Glaciation. The majority of the forest area, included in the Augustów Plain, lies on fluvial and glacial sands and gravels (Lenczewski and Nowakowski, 1999). Lake Wigry is an unusual, mesotrophic lake which consists of a few basins connected by straights which together with bays and islands divide water masses into several water regions (Kamiński, 1999). The Wigry National Park is a unique ecosystem of water and land. The flora of the Wigry National Park comprises about 800 species of vascular plants, 200 species of the Phylum bryophyta and 300 species of lichens, 47 legally protected species (Lenczewski and Nowakowski, 1999; Sokołowski and Kot, 1996). The results of measurements of radiocarbon and stable isotopes in organic and carbonate fractions of the Wigry Lake sediments (Pawlyta et al., 2004) gives a chance to study temporal behaviour of a lacustrine ecosystem and its dynamics.

Lake Gościąż (**Fig. 2**) is situated in the Vistulian River Valley between Płock and Włocławek and it belongs to the drainage basin of the Ruda which is the left tributary of the Vistula (Churski and Marszelewski, 1998). Lake Gościąż (52°35'N, 19°21'E) is the north-western part of Gostyń Lake District.

The system of four lakes called "Na Jazach" and the stream Ruda connecting the lakes were the object of the floristic and phytosociological field research, together with the surrounding forest areas and nearest peatbogs. The interdisciplinary systematic isotopic investigation studies



Fig. 1. Location of Wigry Lake and sampling sites (1-Słupiańska Bay, 2-Wigierka Bay, 3- Ostrów Island, 4-Black Lake nearby Gawrych Rudy, 5-Samle Mate Lake, 6-Samle Duże Lake, 7-Sielawa Góra Shallow 8-Nearby Krowa Island).



were started in 1987 and continued until 1994 (Goslar et al., 1992; Ralska-Jasiewiczowa et al., 1998).

The results of measurements of radiocarbon and stable isotopes in organic and carbonate fractions of the laminated sediment of Gościąż Lake (Ralska-Jasiewiczowa *et al.*, 1998) enabled to reconstruct the behaviour of lake level fluctuation in the past.

The flora of the "Na Jazach" lake includes 560 species of vascular plants belonging to 81 families. Its richness is the consequence of the considerable diversity of habitats. An essential fraction of the flora comprises species adapted to aquatic and submerged. A significant number of vascular plant species present in the Eastern Suwałki Lake District, the Augustowska Plain and Gostyń Lake District is associated with aquatic environment and wetlands. Their existence depends on the diversity of lakes, rivers, water-heads, wet meadows, moors and wet forests.

The vegetation is differentiated according to the prevailing habitat conditions: hydrologic conditions, nutrient resources and topographic features. One of the principal factors affecting the vegetation diversity of the area in question is water originating from the small (66km<sup>2</sup>) catchment area of the Ruda stream and stored in four lakes (Gościąż, Wierzchoń, Brzózka and Mielec) and in the stream flowing through them and discharging into the Vistula River near Dobiegniewo (Pazdur *et al.*, 1995).

#### 3. SAMPLING

The research included different parts of the local ecosystem of the sites under investigation. The samples of annual plants and unidentified plant mixture, shells and water (**Tables 1** and **2**) from Wigry Lake and its environment (**Fig. 1**) were collected in July and August 2002 and July 2003. The plant species were identified by botanists from the Wigry National Park, Poland.

The samples of unidentified plant mixture, shells and water (**Tables 3** and **4**) were collected from Gościąż Lake and its environment (**Fig. 2**) between June 1989 and June 1993. The plant species were identified by botanists from the Władysław Szafer Institute of Botany Polish Academy of Sciences, Cracow, Poland.



Fig. 2. Location of Gościąż Lake and sampling sites.

#### 4. CHEMICAL PRETREATMENT

The chemical pretreatment method depended on the material of the sample. The collected material was divided into two groups: (1) organic samples – plants; and (2) inorganic samples – carbonates deposited on plants, shells and water samples.

Various methods were used to determine the isotopic composition of organic matter and carbonates in the collected samples. Radiocarbon measurements were performed using the gas proportional counters and the liquid scintillation counting technique in Gliwice Radiocarbon Laboratory, Poland. In the case of Wigry Lake,  $\delta^{13}$ C and  $\delta^{18}$ O were measured using the Elemental-Analyzer-Mass-Spectrometer and the Pyrolysis-Gas-Chronomatograph-Mass-Spectrometer in UFZ Centre for Environmental Research, Leipzig – Halle, Germany, whereas in the case of Gościąż Lake,  $\delta^{13}$ C and  $\delta^{18}$ O were determined on dual inlet and triple collector mass spectrometer in Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, Lublin, Poland.

## Preparation of samples for <sup>14</sup>C measurements

The samples were pretreated by the standard procedure used in Gliwice Radiocarbon Laboratory (Pazdur *et al.*, 1995; Pazdur and Pazdur, 1986; Goslar, 1981). In the initial stage of preparation, the fresh plants were dried, weighted and then separated from the carbonates. The samples were treated with HCl to remove carbonates. During this treatment, the decrease of the weight was between 20 and 70% and did not depend on temperature. During treatment of samples at 20°C, the reaction proceeded slowly and the preparation time was longer but the same decrease of weight was observed as at 80°C. In the next step of preparation, the samples were subjected to carbonization during which the volatile and the pitchy components, oils, esters and hydrocarbons were removed.

The DIC from water samples was precipitated by treating with a solution of ferrous sulphate, solution of sodium hydroxide, solution of barium chloride and solution of *preastol* (at room temperature). Subsequently, samples were decomposed in a suitable vacuum line.

Collection date	Lab no	Sample name	Plant-species	Fraction	Whole material	Whole material	Alpha-cellulose/ carbonate	Sample description
					<sup>14</sup> C (pMC)	$\delta^{13}$ C (‰ PBD)	$\delta^{18}$ O (‰ SMOW)	
Site: Słupiańska	Bay							
02 Jul 25		WZST/RL/02/1	Sphagnum sp	0		$-27.12 \pm 0.90$	$24.26 \pm 0.52$	wetland
02 Jul 25	Gd-11715	WZSL/RL/02/3	Hypogymnia physodes	0	126.07±0.51	-25.58±0.78	26.47±0.33	terrestrial
02 Jul 25	Gds- 276	WZSL/RL/02/4	Pinus sylvestris	0	$111.52 \pm 0.80$	$-26.15 \pm 0.08$	27.26±0.47	terrestrial
03 Jul		WZS/RL/03	Pinus sylvestris (needles)	0		-26.76±0.03	29.80±0.15	terrestrial
03 Jul		WZS/RL/03/02	Pinus sylvestris (twigs)	0		-27.07±0.07	$28.01 \pm 0.42$	terrestrial
02 Jul 29	Gds-277	WZS/RZ/02/1	Phragmites communis	0	110.34±0.79	-24.95±0.17	26.89±0.22	semi submerged
02 Jul 29		WZS/RZ/02/2	Scirpus lacustris	0		$-27.60 \pm 0.31$	$26.62 \pm 0.11$	semi submerged
02 Jul 29		WZS/RZ/02/2K	Scirpus lacustris	0		$-27.16 \pm 0.38$	$36.92 \pm 0.86$	semi submerged
02 Jul 29		WZS/RW/02/3	Sphagnum	0		$-29.00 \pm 1.10$	$19.31 \pm 0.05$	submerged
02 Jul 29		WZS/RW/02/5	Ceratophylum demersum	0		-15.82±0.66	$20.42 \pm 0.05$	submerged
02 Jul 29	Gd-16204	WZS/RW/02/1	Chara	0	97.10±1.10	$-18.00 \pm 0.06$	20.81±0.26	submerged
03 Jul		WZS/RW/03/03	Fontinalis antipyretica	0		$-28.04 \pm 0.73$		submerged
03 Jul		WZS/RW/03/02	Unidentified	0		$-27.07 \pm 0.07$		submerged
02 Jul 29		WZS/RW/02/2	Stratioides aloides	0		$-15.02 \pm 0.70$	$29.08 \pm 0.36$	submerged
02 Jul 29 depos. on plants		WZS/RW/02/2w	Stratioides aloides	С		-2.23±0.10	21.87±0.01	carbonates
03 Jul	Gd-15632	WZS/RW/03 org	Unidentified	0	90.80±1.10	$-22.50 \pm 0.15$	20.83±0.46	submerged
Site: Wigierka Ba	y							
02 Jul 27	Gd-15579	WZW/RZ/02/1	Nuphar luteum	0	$102.08 \pm 0.97$	$-26.43 \pm 0.12$	$21.03 \pm 0.19$	semi submerged
02 Jul 27		WZW/RW/02/1	Potamogeton perfoliatus	0		-16.25±0.25	20.46±0.18	submerged
02 Jul 27		WZW/RW/02/1w	Potamogeton perfoliatus	С		-2.87±0.02	21.81±0.09	carbonates depos. on plants
03 Jul		WZW/RW/03	Myriophyllum spicatum	0		-20.36±0.27	20.62±0.27	submerged
03 Jul	Gds-273	WZW/RW/03w	Myriophyllum spicatum	С	94.42±0.74	-2.43±0.07	21.76±0.07	carbonates depos. on plants
Site: Ostrów Islar	nd							
02 Jul 27	Gd-11714	WPK/RW/02/1	Potamogeton pectinatus, Chara	0	$106.73 \pm 0.44$	-16.21±0.70	$20.31 \pm 0.32$	submerged
2 Jul 27		WPK/RW/02/1w	Potamogeton pectinatus, Chara	С		-2.42±0.08	21.63±0.05	carbonates depos. on plants
Site: Black Lake I	nearby Gawrych	Rudy						
03 Jul		WJCz/RW/03/01	Carex	0		$-27.51 \pm 0.10$	25.45±0.17	submerged
03 Jul		WJCz/RW/03/02	Phragmites communis	0		-24.63±0.26	27.88±0.11	submerged
03 Jul		WJCz/RW/03/02w	Phragmites communis	0		-23.39±0.11	$28.95 \pm 0.05$	submerged
03 Jul		WJCz/RW/03/03	Unidentified mixture	0		$-23.61 \pm 0.20$	29.05±0.38	submerged
02 Aug 03		WJCz/RW/02	Unidentified	0		-31.20±1.70	16.25±0.68	submerged
02 Aug 03		WJCz/RW/02w	Unidentified	С		-8.68±0.05	$20.12 \pm 0.05$	carbonates depos. on plants
Site: Samle Małe	Lake							
02 Jul 26 Site: Samle Duže I	Gd-30034	WSM/RW/02/1	Chara	0	89.07±0.88	$-29.00\pm2.50$	17.96±0.17	submerged
02 Jul 26	Gd-18225	WSD/RW/02/1	Myriophyllum spicatum	0	112.70±2.10	-26.41±0.09	19.37±0.13	submerged
02 Jul 26		WSD/RZ/ 02/1	Carex acutifornis	0		-28.05±0.09		semi submerged
Site: Sielawa Gór	a Shallow	· · ·						<u> </u>
03 Jul		WSG/RW/03 org	Unidentified	0		-24.12±0.34	21.85±0.03	submerged

Table 1.	Results of <sup>14</sup> C.	$\delta^{13}C$ and $\delta^{18}O$ measurements in	plants and carbonates de	eposited on	plants collected from	n Wiarv Lake.
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After physical examination and cleaning of the surface, the shells were treated with HCl in order to remove the outer layers of shells.

After the chemical pretreatment,  $CO_2$  was produced from organic samples by combustion in temperature ca 1000°C, and from carbonates by decomposition with 10% HCl. Both processes were carried out in vacuum lines.

#### Preparation of samples for $\delta^{18}O$ and $\delta^{13}C$ measurements

The samples were prepared by the standard procedure used in Centre for Environmental Research, Leipzig – Halle in Germany. The initial stage of the process was sample milling into pieces of a size less than 0.5 mm and treatment with a benzene-methyl alcohol mixture (in proportion 1:1). The reaction was performed in a special testtube at 40°C over 6h. Afterwards, the samples were treated with acetone for 1h and subsequently dried overnight. The following step was bleaching with NaClO<sub>2</sub> and CH<sub>3</sub>COOH solution at 60°C for 36h in order to remove lignin and to extract cellulose. The resultant cellulose was rinsed with boiling distilled water, treated with NaOH for 4h and rinsed with distilled water at room temperature, and dried overnight at 50°C.

After the pretreatment with NaClO<sub>2</sub>, the carbonates deposited on plants were rinsed, dried at a temperature of 105°C, and leached in a vacuum apparatus.

## 5. MEASUREMENTS OF ISOTOPE CONCENTRATIONS

There are five custom designed gas proportional counters (GPC) and one commercial liquid scintillation  $\beta$  spectrometer (LSC) Quantulus  $1220^{\text{TM}}$  in the Gliwice Radiocarbon Laboratory. The counting rates for a sample and standard of contemporary biosphere are proportional to the concentration of radiocarbon in the sample and standard respectively (Pazdur *et al.*, 2003; Pazdur *et al.*, 2000). Three counting geometries are applied in Quantulus  $1220^{\text{TM}}$ : 3 ml, 2 ml and 0.8 ml (Pawlyta *et al.*, 1998), and the benzene may be obtained from samples containing respectively 2.43 g, 1.62 g and 0.65 g of pure carbon when assuming no loss of carbon during benzene synthesis (Pazdur *et al.*, 2003). As a reference material "ANU Sucrose" was used.

Stable isotopes for Wigry Lake were measured in the UFZ Centre for Environmental Research, Leipzig-Halle.  $\delta^{13}$ C in plants was measured using the EuroVector 3000 Elemental Analyzer coupled to DELTA<sup>PLUS</sup>XP via the ConFlow III (ThermoFinningan, Bremen) using the technique based on "dynamic flash combustion" method and subsequent isotope analysis of carbon dioxide.  $\delta^{13}$ C in carbonates and  $\delta^{18}$ O were measured using a DELTA<sup>PLUS</sup>XL spectrometer (ThermoFinnigan, Bremen). High temperature pyrolisis (HTP) was carried out on the HEKAtech Wegberg pyrolisis reactor connected to the DELTA<sup>PLUS</sup>XL with the ConFlow III (Hecarrier gas). In these measurements, ANU Sucrose, KH2 (BaCO<sub>3</sub>) and MKC reference materials were used.

## 6. DISCUSSION OF RESULTS

<sup>14</sup>C, δ<sup>13</sup>C and δ<sup>18</sup>O records for Wigry Lake are presented in order of investigated sites in **Tables 1** and **2**, and δ<sup>13</sup>C and δ<sup>18</sup>O values in plants in **Table 3**, the total content of carbon in plant records in **Table 4**. For comparison, Gościąż Lake records are given in **Table 5** and **Table 6** in order of collection date.

#### $\delta^{_{13}}C$ in lacustrine environment

The results of  $\delta^{13}$ C measurement values in plants and associated carbonates are presented in Fig. 3 in order of vegetation conditions (Tables 1, 2, 5 and 6). Straight lines indicate weighted average (Table 7a). In Wigry Lake, we can observe higher average  $\delta^{13}$ C values than in Gościąż Lake.

However, the lowest  $\delta^{13}$ C mean values (**Table 7a**) are observed in the group of wetland and semi submerged plants, higher in the group of terrestrial plants, and the highest in submerged plants. It should be noted that  $\delta^{13}$ C variability (**Fig. 3**) is ca 2.5‰ in Wigry Lake and ca 5‰ in Gościąż Lake is observed in terrestrial plants, while the variability in semi submerged plants reaches ca 4‰ in both lakes, and the  $\delta^{13}$ C of submerged plants shows variability of ca 16‰ in Wigry Lake and ca 22‰ in Gościąż Lake.

If the  $\delta^{13}$ C mean values in carbonates from Wigry Lake are concerned, the lowest level is observed in DIC, higher in shells and in carbonates deposited on plants. In Gościąż Lake we observe that average  $\delta^{13}$ C values in carbonates are the lowest in shells, higher in DIC and in carbonates deposited on plants.

In Wigry Lake, the shells show a variability of ca 1‰, the carbonates deposited on plants ca 6‰ (if we exclude one extreme result for unidentified mixture then the variability is ca 0.5‰ and the weighted average in this group is equal to -2.84‰), and DIC show variability of ca 0.6‰. It is observed that  $\delta^{13}$ C mean values in carbonates are much lower than in plants.

In Gościąż Lake, the carbonates deposited on plants show variability of ca  $1\%_o$ , from plants variability of ca  $4\%_o$  (if we exclude one extreme result for unidentified mixture then the variability is ca  $1.5\%_o$  and weighted average in this group is equal to  $-3.97\%_o$ ), and DIC shows variability of ca  $12\%_o$ .

In general, it is observed that  $\delta^{13}C$  mean values in DIC are much lower then in carbonates deposited on plants.

The results presented at **Fig. 4** can be interpreted in many different ways, e.g. according to class division.

#### $\delta^{13}C$ in plants in the Gościąż Lake environment

The results of  $\delta^{13}$ C measurements in *Pinopsida* (Class) indicate different level of  $\delta^{13}$ C in one species. It should be noted that one of these samples was collected in 1990 and the others in 1991 from different parts of the forest (**Table 5**). In *Liliopsida* (Class), 3 groups of plants can be distinguished. The first group, with the highest  $\delta^{13}$ C level, contains *Stratioides aloides, Potamogeton* and *Potamogeton lucense*. The  $\delta^{13}$ C values of these species show variability from -18.5 to -13% $\sigma$ , and in *Stratioides aloides* we observed

**Table 2.** Results of <sup>14</sup>C,  $\delta^{13}$ C and  $\delta^{18}$ O measurements in DIC and shells collected from Wigry Lake.

Collection Date	Lab no	Sample name	Fraction	Whol	e matei	rial-ino	rganic
		•		<sup>14</sup> C (pMC)	δ <sup>13</sup> C (‰ PBD)	δ <sup>18</sup> 0 (‰ SMOW)	Sample description
Site: Nearby Krowa Island							
03 Jul	Gd-18224	WKW/03	С	95.57±1.10	-5.80±1.20	$20.30 \pm 2.80$	DIC
Site: Sielawa Góra							
03 Jul	Gd-18228	WSGW/03	С	$100.30 \pm 1.20$	$-5.53 \pm 0.10$	$26.10 \pm 0.10$	DIC
Site: Słupiańska Bay							
03 Jul		WZSW/03	С		$-5.22 \pm 0.04$	$23.78 \pm 0.06$	DIC
03 Jul	Gd-12594	WZS/RW/03/M W	С	$97.44 \pm 0.94$	-5.31±0.12	$22.98 \pm 0.04$	shells
02 Jul 29		WZS/RW/02/5 M	С		-6.15±0.06	23.46±0.04	shells

**Table 3.** Comparison of  $\delta^{13}C$  and  $\delta^{18}O$  values within parts and components of plants.

Sample name	Species		Whole tissue $\delta^{13}C(\infty \text{ PBD})$	Alpha-cellulose $\delta^{18}O$ (‰ SMOW)	Sample description
WZS/RL/03	Pinus silvestris	Needles	$-26.76 \pm 0.03$	29.80±0.15	terrestrial
WZS/RL/03/02		Twigs	$-27.07 \pm 0.07$	$28.01 \pm 0.42$	terrestrial
WZS/RZ/02/2	Scirpus lacustris	Whole	$-27.60 \pm 0.31$	26.62±0.11	semi submerged
WZS/RZ/02/2K		Flowers	$-27.16 \pm 0.38$	$36.92 \pm 0.86$	semi submerged
WJCz/RW/03/02	Phragmites communis	Whole	$-31.20 \pm 1.74$	16.25±0.68	submerged
WJCz/RW/03/02w		bouquet of flowers	$-23.39 \pm 0.11$	20.12±0.05	submerged









ca 4‰ scatter of results. The second group, with lower level of  $\delta^{13}$ C, contains *Juncus, Phragmanites Communis, Phragmites Australis* and shows a  $\delta^{13}$ C variability from ca -27.7 to -26.5‰. In the third group, with the lowest level of  $\delta^{13}$ C, containing *Acorus calamus, Carex paniculata, Carex Rostata, Carex sp., Typha* and *Typha angustifolia*, the  $\delta^{13}$ C values vary from ca -29 to -31‰.

In the light of the data (**Table 5**, **Fig. 4**) for *Magnoliopsida* (Class) which contains *Betula*, *Betula pubescens*, *Ceratophyllum submersum*, *Frangula*, *Myriophyllum sp.*, a considerable dispersion of experimental values is observed. It can be caused by different sites of plant origin and also by the fact that some of these plants are terrestrial, others are submerged or semi submerged plants, thus the sources of carbon incorporated into the plant tissue are variable as well as they have differ in fractionation during assimilation.

Analysis of vegetation conditions with indicated by sampling sites (**Table 7a**) showed an overall range in  $\delta^{13}$ C values from ca -27.6 to -25% whilst a mean scatter of results is observed in the group of submerged plants (**Fig. 3**). Analysis of  $\delta^{13}$ C in *Algae* showed an overall range in  $\delta^{13}$ C values from ca -35 to -28%.

We can observe that  $\delta^{13}$ C values of plants collected from Wigry Lake are higher then  $\delta^{13}$ C values of the same species collected from Gościąż Lake. The difference in  $\delta^{13}$ C values of plants growing under similar conditions could be explained by various possible reasons. First, different species are known to have different isotopic composition. Second, various photosynthesizing parts of plants show a range of  $\delta^{13}$ C values. Third, the physiognomy of the plants could also be an important factor in explaining the isotopic differences. Most probably the observed effects are due to all these reasons and at this stage of research it is difficult to indicate unambiguously the most important reason.

## $\delta^{13}C$ in plants in the Wigry Lake environment

The results of measurements of  $\delta^{13}$ C in *Pinopsida* (Class) indicate variability of  $\delta^{13}$ C in one species - *Pinus silvestris* in different plant components. It should be noted that needles and twigs were separated from samples collected in 2003, and the third sample, collected in 2002, was not subdivided (**Table 1**).

The lowest value of  $\delta^{13}$ C is observed for needles of *Pinus silvestris*. In *Liliopsida* (Class) 3 groups of plants can be distinguished: (1) the first group, with the highest  $\delta^{13}$ C level, which contains *Scirpus lacustris, Stratioides aloides*. The  $\delta^{13}$ C values of these species showed variability from -16 to -15‰; (2) the second group, with lower level of  $\delta^{13}$ C, which contains three samples of *Phragmites comunis*. The  $\delta^{13}$ C values of this species (in whole plants) showed variability from ca -25 to -24‰, and the  $\delta^{13}$ C value of bouquet of flowers is 23.39±0.11‰; and (3) the third group, with the lowest  $\delta^{13}$ C level, which contains *Carex*, *Potamogeton perfoliatus* and mixture of *Potamogeton pectinatus* and *Chara* with  $\delta^{13}$ C variability from ca -26 to -27‰.

In the light of data (**Table 1**, **Fig. 4**) in *Magnoliopsida* (Class) which contains *Nuphar luteum*, *Ceratophylum demersum* and *Myriophyllum spicatum*, a considerable dispersion of measurement results is observed. It can be

**Table 4.** Results of  $\delta^{13}C$  measurements and total carbon content in plants collected from Wigry Lake.

Sample no	Sample name	Plant	δ <sup>13</sup> C (%	• PBD)	Total carb	Total carbon content (%)		
			Whole tissue	Alpha-cellulose	Whole tissue	Alpha-cellulose		
1	WZSL/RL/02/3	Hypogymnia physodes	-25.58±0.78	$-24.93 \pm 0.09$	-	-		
2	WZSL/RL/02/4	Pinus silvestris	$-26.15 \pm 0.08$	$-26.31 \pm 0.05$	45.60	38.30		
3	WZS/RL/03	Pinus silvestris needles	$-26.76 \pm 0.03$	-25.81±0.10	48.70	46.50		
4	WZS/RL/03/02	Pinus silvestris twigs	$-27.07 \pm 0.07$	$-27.00 \pm 0.38$	44.10	47.90		
5	WZS/RZ/02/1	Phragmites communis	$-24.95 \pm 0.17$	$-23.19 \pm 0.04$	46.50	42.60		
6	WZS/RZ/02/2	Scirpus lacustris	$-27.60 \pm 0.31$	-27.05±0.06	42.80	40.40		
7	WZS/RZ/02/2K	Scirpus lacustris flowers	-27.16±0.38	$-25.45 \pm 0.63$	42.80	43.30		
8	WZW/RZ/02/1	Nuphar luteum	-26.43±0.12	-25.98±0.05	47.20	36.60		
9	WZS/RW/02/2	Stratioides aloides	$-15.02 \pm 0.71$	$-15.62 \pm 0.05$	48.10	13.30		
10	WZS/RW/02/5	Ceratophylum demersum	$-15.82 \pm 0.66$	-17.42±0.39	43.70	42.60		
11	WZS/RW/02/1	Chara	$-18.00 \pm 0.06$	$-19.51 \pm 0.02$	25.50	43.90		
12	WZS/RW/03 org	Unidentified	$-22.50 \pm 0.15$	$-21.45 \pm 0.05$	42.40	42.90		
13	WZW/RW/02/1	Potamogeton perfoliatus	$-16.25 \pm 0.25$	-17.86±1.54	39.80	47.70		
14	WZW/RW/03	Myriophyllum spicatum	$-20.36 \pm 0.27$	$-20.47 \pm 0.87$	42.70	48.30		
15	WPK/RW/02/1	Potamogeton pectinatus, Chara	$-16.21 \pm 0.70$	$-15.18 \pm 0.45$	40.60	46.30		
16	WJCz/RW/02	Unidentified	-31.20±1.74	$-34.42 \pm 0.25$	31,90	40,10		
17	WJCz/RW/03/01	Carex	-27.51±0.25	$-25.82 \pm 0.26$	44,40	42,90		
18	WJCz/RW/03/02	Phragmites communis	$-24.63 \pm 0.27$	$-23.94 \pm 0.16$	44,60	45,30		
19	WJCz/RW/03/02w	Phragmites communis	$-23.39 \pm 0.11$	$-22.87 \pm 0.05$	44.40	41.90		
20	WJCz/RW/03/03	Unidentified	$-23.61 \pm 0.20$	$-22.66 \pm 0.09$	38.20	43.40		
21	WSM/RW/02/1	Chara	$-28.98 \pm 2.54$	$-25.45 \pm 0.45$	41.30	41.70		
22	WSD/RW/02/1	Myriophyllum spicatum	$-26.41 \pm 0.09$	-26.42±0.18	38.60	45.30		
23	WSG/RW/03 org	Unidentified	-24.12±0.34	-22.09±0.10	54.20	46.40		

caused by different origin of plants and also by the fact that *Myriophyllum spicatum* and *Ceratophylum demersum* are submerged plants and *Nuphar luteum* is semi submerged plant. Analysis of vegetation conditions indicated by sampling sites (**Fig. 5**, **Table 7a**) showed an overall range in  $\delta^{13}$ C values from ca -28 to -25‰ whilst a mean scatter of results is observed in the group of submerged plants (**Figs 3**, **5** and **6a**).

Analysis of  $\delta^{13}$ C in *Bryophyta* (Subkingdom) which contains different species of moss from wetland and aquatic areas, gives an overall range in  $\delta^{13}$ C values from ca -29 to -27‰, with the lowest level of  $\delta^{13}$ C for *Sphag*- *num* from wetland area nearby Słupiańska Bay (**Table 1**, **Fig. 4**). As far as *Charophycea* (Class) is concerned, the  $\delta^{13}$ C values show different level - the lowest for Samle Małe Lake and the highest for samples collected nearby Ostrów Island and from Słupiańska Bay. For *Lecanoromyales* (Class) we have made analysis only for one sample of lichens and the  $\delta^{13}$ C is equal to ca -26‰.

Analysis of  $\delta^{13}$ C variation in plants in the whole material and in alpha-cellulose (**Fig. 5**) shows in several cases an isotopic depletion or enrichment. In some cases, the  $\delta^{13}$ C values of whole materials are depleted in comparison with cellulose. The possible reason for this is the fact

**Table 5.** Results of <sup>14</sup>C,  $\delta^{13}$ C and  $\delta^{18}$ O measurements in plants and carbonates deposited on plants collected from Gościąż Lake.

Collection date	Lab no	Sample name	Plant-species	Fraction	W h o ∣ ¹⁴C(pMC)	le mater δ <sup>13</sup> C (‰ PBD)	i a l Sample description
89 Jun 21	Gd-5559	GRW-1/89	Betula sp.	0	$120.8 \pm 0.5$	-31.40±0.06	terrestrial
89 Jun 07	Gd-5569	GRW-2/89	Carex sp.	0	$119.1 \pm 0.5$	$-30.83 \pm 0.06$	submerged
90 Mai 28	Gd-4585	GRW-1/90	Stratiotes aloides L.	0	77.8±1.0	$-15.62 \pm 0.06$	submerged
90 Mai 28	Gd-5742	GRW-2/90	Phragmanites communis Trin	0	$118.3 \pm 0.6$	-27.67±0.06	semi submerged
90 Mai 28	Gd-5740	GRW-3/90	Acorus calamus L.	0	115.3±0.6	$-30.91 \pm 0.06$	semi submerged
90 Mai 28		GRW-4/90	Myriophyllum sp.	0	-	-19.46±0.06	submerged
90 Mai 28	Gd-6264	GRW-5/90	Ceratophyllum submersum L.	0	85.3±0.7	-19.67±0.06	submerged
90 Mai 28	Gd-6263	GRW-6/90	Frangula alnus Mill.	0	$115.5 \pm 0.9$	$-27.95 \pm 0.06$	semi submerged
90 Mai 28	Gd-5743	GRW-7/90	Betula pubescens Ehrh.	0	117.4±0.6	-29.28±0.06	semi submerged
90 Mai 28	Gd-5744	GRW-8/90	Pinus silvestris L.	0	118.2±1.1	-28.53±0.06	terrestrial
91 Mar 11	Gd-5914	GRW-1/91	Pinus silvestris L.	0	120.4±1.0	-27.74±0.06	terrestrial
91 Mar 11	Gd-5899	GRW-2/91	Phragmites communis Trin.	0	117.6±1.0	-26.54±0.06	semi submerged
91 Jul 20	Gd-6523	GRW-3/91	Phragmites australis	0	-	$-28.30 \pm 0.06$	wetland
91 Jul 20	Gd-5940	GRW-4/91	Typha angusifolia L.	0	$121 \pm 0.8$	-29.12±0.06	wetland
91 Jul 20	Gd-6472	GRW-5/91	Stratoites aloides L.	0	82.3±1.2	-13.04±0.06	submerged
91 Jul 20	Gd-6471	GRW-6/91	Ceratophyllum submersum L.	0	85.1±1.3	-18.77±0.06	submerged
91 Jul 20	Gd-6476	GRW-8/91	Juncus sp.	0	103.4±1.6	-27.20±0.06	submerged
91 Jul 20	Gd-5949	GRW-9/91	Graminea	0	116.6±0.9	-29.66±0.06	semi submerged
91 Jul 20	Gd-5950	GRW-10/91	Potamogeton lucense L.	0	87.9±0.5	$-18.56 \pm 0.06$	submerged
91 Jul 20	Gd-5951	GRW-11/91	Cladophera glomerata L.	0	92.4±0.6	$-22.00\pm0.06$	submerged
91 Jul 20	Gd-6475	GRW-13/91	Carex paniculata L.	0	113.1±1.0	-29.71±0.06	semi submerged
92 Aug 18	Gd-6699	GRW-4/92	Stratoites aloides	0	85.2±1.2	-17.31±0.06	submerged
92 Oct 03	Gd-6732	GRW-5/92	Unidentified	0	118.6±1.6	$-29.89 \pm 0.06$	semi submerged
92 Oct 03	Gd-7183	GRW-6/92/C	Unidentified	С	97.3±1.0	-4.82±0.06	carbonates dep. on plants
92 Oct 03	Gd-7198	GRW-6/92/0	Byrophyta Algae	0	85.9±0.8	$-35.01 \pm 0.06$	submerged
92 Oct 03	Gd-4890	GRW-7/92	Algea	0	74.2±1.9	-31.98±0.06	submerged
92 Oct 03	Gd-4892	GRW-8/92	Potamogeton	0	74.0±1.7	$-18.50 \pm 0.06$	submerged
92 Oct 03	-	GRW-13/92	Carex sp	0	113.5±0.6	$-30.15 \pm 0.06$	wetland
92 Oct 03	Gd-4893	GRW-15/92	Cladophera sp.	0	91.2±1.5	-30.16±0.06	submerged
92 Oct 03	Gd-7182	GRW-1/92/C	Unidentified	С	88.6±0.8	$-3.60 \pm 0.06$	carbonates
92 Oct 03	Gd-7199	GRW-1/92/0	Betula	0	119.4±0.6	-26.61±0.06	semi submerged
93 Jun 18	Gd-6929	GRW-2/93	Carex Rostata Stokes	0	116.8±1.4	$-30.00 \pm 0.06$	wetland
93 Jun 19	Gd-7406	GRW-5/93	Alga	0	64.8±1.0	$-32.00 \pm 0.06$	submerged
93 Jun18	Gd-6928	GRW-7/93	Carem paniculata L.	0	129.5±1.6	-29.70±0.06	submerged
93 Jun 18	Gd-6931	GRW-14/93/0	Algae+Detrytus	0	102.2±1.2	$-28.00 \pm 0.06$	submerged
93 Jun 18	Gd-7397	GRW-14/93/C	Unidentified	С	79.7±0.6	$-3.50 \pm 0.06$	carbonates
93 Jun 18	Gd-6895	GRW-14/93/C-M	Shells	С	89.9±1.4	-8.21±0.06	shells
93 Jun 18	Gd-7374	GRW-18/93/C	Unidentified	С	79.0±0.5	$-1.03 \pm 0.06$	submerged
93 Jun 18	Gd-6927	GRW-18/93/0	Algae	0	79.4±1.5	-29.93±0.06	submerged
93 Jun 18	Gd-6933	GRW-19/93	Typha	0	107.3±1.5	-29.00±0.06	semi submerged
93 Jun 18	Gd-7424	GRW-20/93	Carex Rostata Stokes	0	107.3±0.9	$-30.00 \pm 0.06$	semi submerged
93 Jun 18	Gd-9133	GRW-21/93	Heleocharis palustris (L)	0	120.4±3.4	$-30.00 \pm 0.06$	semi submerged

that the other chemical components, such as lipids, are known to be isotopically depleted compared to cellulose (Deines, 1980; Rajagopalan *et al.*, 1999; Raven *et al.*, 1993). If  $\delta^{13}$ C values of whole materials are enriched compared to that of cellulose, the reason is difficult to explain at this stage of research. In several samples, the carbon content in whole tissue is lower than in alpha-cellulose. In the case of *Stratioites aloides*, we observe much lower value of carbon content in alpha cellulose than in the whole tissue, while in *Chara* we observe very low carbon content in the whole tissue, and much higher in alpha-cellulose.



**Fig. 5.** Wigry Lake.  $\delta^{13}C$  values in plants for whole tissue and alpha-cellulose.

**Table 6.** Results of <sup>14</sup>C,  $\delta^{13}$ C and  $\delta^{18}$ O measurements in DIC and shells collected from Gościąż Lake.

Collection	Lab no	Sample name	Fraction				
Date				¹⁴C (pMC)	δ¹³C (‰ PBD)	δ¹80 (‰ SMOW	<ol><li>Sample description</li></ol>
89 Jun 06		GWW-1/89	С	$70.0 \pm 4.0$	$-10.69 \pm 0.06$	$10.3 \pm 0.2$	DIC
89 Jun 06		GWW-2/89	С	$64.5 \pm 2.7$	-5.59±0.06	$19.9 \pm 0.2$	DIC
89 Jun 06		GWW-3/89	С	63.4±1.1	-10.14±0.06	$20.1 \pm 0.2$	DIC
89 Jun 06		GWW-5/89	С	$63.0 \pm 3.3$	-9.28±0.06	18.8±0.2	DIC
89 Jun 06		GWW-6/89	С	69.2±1.4	-17.07±0.06	18.7±0.2	DIC
89 Jun 06		GWW-1/91	С	78.8±0.7	-8.78±0.06		DIC
91 Mar 04	Gd-4705	GWW-2/91	С	86.2±1.6	-8.96±0.06		DIC
91 Jul 20	Gd-4753	GWW-3/91	С	98.8±2.6	-12.69±0.06		DIC
91 Jul 20	Gd-4760	GWW-1/92	С	71.3±0.5	-11.23±0.06		DIC
92 Oct.03	Gd-4887	GWW-2/92	С	83.1±0.8	-10.94±0.06		DIC
92 Oct.03	Gd-4891	GWW-1/93	С	44.3±0.8	-7.67±0.06		DIC
93 Jun 05	Gd-9029	GWW-2/93	С	95.9±2.7	-10.00±0.06		DIC
93 Jun 05	Gd-6984	GWW-3/93	С	87.4±1.2	-8.04±0.06		DIC

**Table 7a.** Average values of  $\delta^{13}C$  in plants and associated carbonates. "n" indicates the number of samples.

	Wigry Lake		Gościąż Lake	
Sample	δ <sup>13</sup> C (‰ PDB)	n	δ <sup>13</sup> C (‰ PDB)	n
Terrestrial plants	$-26.74 \pm 0.035$	4	$-28.57 \pm 0.06$	4
Wetland plants	$-27.12 \pm 0.90$	1	$-29.35 \pm 0.06$	5
Semi submerged plants	-27.11±0.13	5	$-28.98 \pm 0.06$	12
Submerged plants	$-22.98 \pm 0.10$	18	$-24.57 \pm 0.06$	16
Carbonates (depos. on plants)	$-3.306 \pm 0.002$	5	$-3.24 \pm 0.06$	4
Carbonates (shells)	$-5.96 \pm 0.072$	2	$-8.21 \pm 0.06$	1
Carbonates (water) DIC	$-5.08 \pm 0.046$	3	$-10.01 \pm 0.06$	13

The carbon content (**Table 4**, **Fig. 6**) shows variations from 25 % in *Chara* to 54% in unidentified mixture of plants.  $\delta^{13}$ C versus content of total carbon is presented in **Figs 7** and **8**. The average value of total carbon content in whole tissue is equal to 43.6±5.8% and in alpha-cellulose 42.16±7.0%.

Figs 8a-b present values of  $\delta^{13}$ C of photosynthetically fixed carbon for four groups of plants: terrestrial plants, wetland plants, semi submerged plants and submerged plants. The values of  $\delta^{13}$ C among terrestrial and semi submerged plants are lower than -25% PDB, while a considerable scatter of results is observed in the group of submerged plants. This phenomenon can be connected with the hydrological conditions of the given lake (Deines, 1980; Rajagopalan *et al.*, 1999; Raven *et al.*, 1993) and has not been explained yet.

**Table 7b.** Average values of  $\delta^{18}$ O in plants and carbonates.

Sample	δ <sup>18</sup> 0 (‰ SMOW)	n
Wigry Lake		
Terrestrial plants	28.98±0.22	4
Wetland plants	$24.26 \pm 0.52$	1
Semi submerged plants	26.81±0.15	3
Submerged plants	$24.615 \pm 0.006$	16
Carbonates (dep.on plants)	21.79±0.02	5
Carbonates (shells)	$22.983 \pm 0.004$	2
Carbonates (DIC in water)	$24.41 \pm 0.07$	3
Gościąż Lake		
Carbonates (DIC in water)	19.56±0.06	5

## $\boldsymbol{\delta}^{\scriptscriptstyle 18}O$ in lake environment

The results of  $\delta^{18}$ O measurements in alpha-cellulose, which are listed in **Table 1**, are presented in **Figs 9-10**. The results of  $\delta^{18}$ O measurements in plants and in associated carbonates divided according to vegetation conditions (**Table 1**) are presented in **Fig. 9**. Straight lines indicate weighted average in Wigry Lake, and dashed lines - in Gościąż Lake. These values are listed in **Table 7b**.

The highest level of average  $\delta^{18}$ O values (**Table 7b**) is observed in the group of terrestrial plants, lower in group of semi submerged plants, and the lowest in the group of submerged and wetland plants. As far as carbonates are concerned, the highest level is observed in the group of DIC, lower in shells and the lowest in the group of carbonates collected from plants.

The variability of  $\delta^{18}$ O values (**Fig. 9**) in terrestrial plants is ca 3‰, in semi submerged plants ca 16‰, in submerged plants 9‰. As far as the  $\delta^{18}$ O values in carbonates are concerned, the shells showed variability of ca 0.5‰, and DIC 6‰. The carbonates from plants show variability of ca 2‰ and if we exclude one extreme result for unidentified mixture then the variability is ca 0.8‰. The extreme results of  $\delta^{13}$ C and  $\delta^{18}$ O values are observed in the same sample and they appear on both figures (**Figs 3** and **9**).

The results presented in **Fig. 10** can be interpreted in many different ways, e.g. according to class of plants. The  $\delta^{18}$ O values in *Pinopsida* (Class) indicate variable levels of  $\delta^{18}$ O in one species - *Pinus silvestris* in different plant components. Comparing these values one can observe, that twigs have a lower  $\delta^{18}$ O value than needles of *Pinus silvestris* and similar depletion is observed for  $\delta^{13}$ C.



*Fig. 6.* Wigry Lake. Comparison of total carbon content in whole tissue of plant and in alphacellulose.

Two groups of plants can be distinguished in *Liliopsida* (Class): the first group, with the highest level of  $\delta^{18}$ O, which contains *Phragmites communis*, *Stratioides aloides*, *Scirpus lacustris* and *Carex*. The  $\delta^{18}$ O values of these species show variability from *ca* 26.6 to 28%o. The  $\delta^{18}$ O value of *Scirpus lacustris* bouquet of flowers is higher and is equal to 37%o. The second group, with lower level of  $\delta^{18}$ O, which contains *Potamogeton perfoliatus* and mixture of *Potamogeton pectinatus* and *Chara*, has  $\delta^{18}$ O values in whole plants from ca 20.31 to 20.46%o.

In the light of the data (**Table 1**, **Fig. 10**) in *Magnoliopsida* (Class) which contains *Nuphar luteum, Ceratophylum demersum, Myriophyllum spicatum*, a variability of  $\delta^{18}$ O from ca 19.37 to 21.03‰ can be observed. The  $\delta^{13}$ C are slightly scattered in this Class (**Fig. 6**).

Analysis of  $\delta^{18}$ O in *Bryophyta* (Subkingdom) which contains different species of moss from wetland and aquatic areas, showed differences in  $\delta^{18}$ O values and a large scatter from ca 19 to 24% with a variability of ca 2% (**Fig. 10**). The lowest level of  $\delta^{18}$ O is observed for mosses from aquatic area of Słupiańska Bay (**Table 7**).

When *Charophycea* (Class) is concerned, the  $\delta^{18}$ O values show variability from ca 18 to 21%, while  $\delta^{13}$ C showed a large scatter of results.

For *Lecanoromyales* (Class) we have analyzed only one sample of lichens and the  $\delta^{18}$ O is equal to  $26.5 \pm 0.3\%$ .

The difference in  $\delta^{18}$ O values of plants growing under similar conditions can be due to the same reasons as difference in  $\delta^{13}$ C.

Comparison of  $\delta^{13}$ C and  $\delta^{18}$ O in plants is presented in **Fig. 12**. One can observe that samples are divided in three groups according to variability and carbon and oxygen isotope composition: carbonates ( $\delta^{18}$ O between ca 20 and 26‰,  $\delta^{13}$ C between ca -2 and -8‰), submerged plants (with one exception of a semi submerged plant - *Nuphar luteum*;  $\delta^{18}$ O between ca 19 and 22‰;  $\delta^{13}$ C between ca -16 and -29‰) and the group of all types of plants (terrestrial, semi submerged and submerged -  $\delta^{18}$ O between ca 25 and 30‰;  $\delta^{13}$ C between ca 23 and 30‰). The exceptions are two plants – submerged - *Stratioides aloides* and semi submerged – *Scirpus lacustris* (flowers).

Comparison and differences in  $\delta^{13}$ C and  $\delta^{18}$ O within plants in the whole material and in alpha-cellulose are presented in **Table 3**. Few samples are isotopically depleted and the others are enriched. Possibly these effect are due to physiognomy and chemical composition of plants, but at this stage of research it is difficult to explain the reasons.



**Fig. 7.** Dependence between  $\delta^{13}C$  values and total carbon content in plants. (R<sup>2</sup>-squared of correlation coefficient; the trend lines: straight line - alpha cellulose and dashed line - whole tissue).

Table 8. Average <sup>14</sup>C concentration in plants and associated carbonates ordered according to vegetation conditions.

	Wigry Lake		Gościąż Lake	
Sample	<sup>14</sup> C (pMC)	n	<sup>14</sup> C (pMC)	n
Terrestrial plants	$121.86 \pm 0.59$	2	$120.36 \pm 0.67$	3
Wetland plants	-	-	$116.26 \pm 0.75$	4
Semi submerged plants	107.04±0.86	2	$116.19 \pm 0.76$	12
Submerged plants	$103.92 \pm 0.65$	5	92.99±0.81	17
Carbonates (dep. on plants)	94.42±0.74	1	82.82±0.64	4
Carbonates (shells)	107.73±0.96	1	89.89±1.40	1
Carbonates (water)	97.80±1.10	2	71.84±0.88	13

## <sup>14</sup>C in lacustrine environment

The results of <sup>14</sup>C measurement in plants and associated carbonates ordered to vegetation conditions (**Tables 1, 2, 5** and **6**) are presented in **Fig. 9**. Straight lines indicate weighted average. The numerical values with weighted errors are listed in **Table 8**.

In Wigry Lake, the highest level of <sup>14</sup>C is observed in the group of terrestrial plants and lower values in semi submerged and submerged plants. The lowest <sup>14</sup>C concen-

**Table 9.** Average expected values of radiocarbon activity in organic and carbonate fractions of surface lacustrine sediments.

Wigry Lake			Gościąż Lake		
Fraction	<sup>14</sup> C (pMC)	n	<sup>14</sup> C (pMC)	n	
Organic	$109.17 \pm 0.68$	9	$112.60 \pm 0.80$	36	
Inorganic	$96.30 \pm 0.92$	4	80.33±0.81	18	

tration is in the group of carbonates deposited on plants. As it was mentioned above, all organic samples were annual plants which form the lacustrine sediments.

The <sup>14</sup>C concentration (**Fig. 13**) shows variability of ca 25 pMC in terrestrial plants, ca 8 pMC in semi submerged plants and 23 pMC in submerged plants. The <sup>14</sup>C concentration in carbonates (DIC) shows variability of ca 4.5 pMC. The activity of annual shoots of Scots pine corresponds to radiocarbon activity in the atmosphere at the time of collection of samples. The level of <sup>14</sup>C is higher than activity of radiocarbon in atmosphere before 1950 (before nuclear power generation). In 2002, this value was higher by ca 11%. This fact indicates that the "bomb effect" is clearly observed in modern annual plants. Considering the sample material in Gościąż Lake, we observe the same trends in the <sup>14</sup>C concentration. The <sup>14</sup>C concentration (**Fig. 12**) shows variability of ca 2 pMC in terrestrial plants, ca 6 pMC in wetland plants,



**Fig. 8a.** Wigry Lake.  $\delta^{13}C$  values of photosynthetically fixed carbon. The values of  $\delta^{13}C$  among terrestrial and semi submerged plants are lower than -25%; the considerable scatter of results is observed for submerged plants.

**Fig. 8b.** Gościąż Lake.  $\delta^{13}C$  values of photosynthetically fixed carbon. The values of  $\delta^{13}C$  among terrestrial and semi submerged plants are lower than -27‰; the significant scatter of results is observed in submerged plants.



**Fig. 9.**  $\delta^{18}$ O values in plants and carbonates in order of vegetation conditions. Straight lines indicate weighted average values in Wigry Lake, and dashed lines - in Gościąż Lake.



**Fig. 10.** Wigry Lake.  $\delta^{18}$ O values in plants and lichens with syntaxonomic division.



**Fig. 11.** Comparison of  $\delta^{13}C$  and  $\delta^{18}O$  values in plants and carbonates.

ca 19 pMC in semi submerged plants and 65 pMC in submerged plants. The variability is caused by hydrological conditions of the lake. The "bomb effect" is also observed in annual plants from Gościąż Lake.

A lower value (but still higher than 100%) is observed in semi submerged plants and submerged plants in the case of Wigry Lake, as well as in wetland and semi submerged plants from Gościąż Lake indicates the so-called reservoir effect, caused by differentiation of sources of carbon incorporated into plant tissue (i.e. atmospheric CO<sub>2</sub> or DIC).

The dilution factors and reservoir ages calculated for sample from Wigry Lake and its environment are listed in **Tables 10** and **11**. The results for submerged plants from Samle Duże Lake, carbonates from Słupiańska Bay and Sielawa Góra Lake are also included in **Table 10**. The sediment cores were sampled from the last two sites.

The reservoir age  $T_R$  of the organic fraction of Wigry Lake sediments is equal to  $171\pm76$  years and the carbonate fraction reservoir age is equal to  $1179\pm96$  years. The reservoir effect in the youngest sediments is  $500\pm200$ years for the organic fraction and  $2000\pm280$  for carbonate fraction from Słupiańska Bay and  $1600\pm40$  years for carbonates fraction from Sielawa Góra. The dilution factors in organic sediments from Samle Duże Lake are lower than average value in Wigry Lake, however radiocarbon activity in *Myriophyllum Spicatum* is characterized by a high value of  $112.7\pm2.1$  pMC (**Tables 1** and **2**).

As it was mentioned above, all plant samples and carbonates will constitute the lake sediment. The mean expected values of radiocarbon activity in organic and carbonate fraction of surface lacustrine sediments calculated on the basis of measurements for modern samples are presented in **Table 10**. The calculation took into account only one year (annual plants were collected in 2002 and 2003) and reflects the ratio of carbonates to organic fraction in the recent lacustrine sediments. The thickness of strata of samples from sediment core from Wigry Lake is 10 cm and assuming the sedimentation rate of 0,33mm/ year, we can calculate that lacustrine gyttja have been formed for 303 years, what leading to the conclusion that the influence of thermonuclear tests effect in this core cannot be observed.

Dilution factors (q) were calculated on the basis of relation:

$$q_0 = \frac{A_0}{S_0} \tag{6.1}$$

$$q_I = \frac{A_0}{S_I} \tag{6.2}$$

where:

 $S_0$  is the activity of the modern standard

 $A_0$  is the initial activity of the sample (fraction)

Values of dilution factors were calculated for  $S_1$  values listed below:

Site	S <sub>o</sub> (pMC) in 1950 year	S <sub>1</sub> (pMC)	
Wigry Lake	100 pMC	$111.52 \pm 0.80$	Pinus sylvestris
			(annual shoot), 2002
Gościąż Lake	100 pMC	$120.40 \pm 1.00$	Pinus sylvestris
			(annual shoot), 1991

The results shown in **Fig. 13** can be interpreted in many different ways. Plants are grouped by species (syntaxonomically division) with indication of sampling sites. Analysis of radiocarbon isotope in the organic fraction from Wigry Lake and its environment (**Table 1**) shows that lichens have the highest and samples of *Chara* have the lowest <sup>14</sup>C concentration.

Table 10. Reservoir effect in plants and carbonates from Gościąż Lake and Wigry Lake.

Fraction	<sup>14</sup> C (pMC)	q <sub>o</sub>	<b>q</b> <sub>1</sub>	δ <sup>13</sup> C (‰ PDB)	T <sub>R0</sub> (yr)	T <sub>R1</sub> (yr)
Gościąż Lake						
Organic	112.6±0.80	$1.126 \pm 0.008$	$0.935 \pm 0.007$	$27.81 \pm 0.06$	Modern	$539 \pm 60$
Carbonates	80.33±0.81	$0.803 \pm 0.008$	$0.667 \pm 0.019$	$-8.41 \pm 0.06$	$-1760 \pm 390$	$3260 \pm 230$
Wigry Lake						
Organic	109.17±0.68	$1.092 \pm 0.007$	$0.979 \pm 0.009$	$-26.29 \pm 0.06$	Modern	171±76
Carbonates	96.30±0.92	$0.963 \pm 0.009$	$0.864 \pm 0.010$	$-3.309 \pm 0.002$	303±77	1179±96
WSD/RW/02/1 submerged plant-organic	112.70±2.10	1.127±0.021	$1.011 \pm 0.030$	$-26.41 \pm 0.09$	Modern	Modern
WZS/RW/03/M W carbonates (shells)	97.44±0.94	0.974±0.009	0.874±0.015	-4.70±1.50	212±74	1080±140
WSGW/03 DIC in water	100.30±1.20	1.003±0.012	$0.899 \pm 0.017$	-5.53±0.10	Modern	860±150

**Table 11.** Reservoir effect in sediment cores; thickness of sediment samples is equal to 10 cm; the sedimentation rate 0.33mm/year (Pawlyta et al., 2004).

Core name	Fraction	q	δ <sup>13</sup> C (‰ PDB)	T <sub>R</sub> (yr)
WSD/412/02	Organic	$0.934 \pm 0.017$	-26	$500 \pm 200$
WZS/406/02	Carbonate	$0.780 \pm 0.027$	-4.0	$2000 \pm 280$
WSG/411/02	Carbonate	$0.819 \pm 0.004$	-2.75	$1600 \pm 40$















Fig. 14. <sup>14</sup>C concentration and total carbon content in plants. Average value of TCC is equal to  $42.0 \pm 6.8\%$ . Straight line indicates mean values of carbon content and dashed lines indicate ranges of one standard error.

The results of <sup>14</sup>C measurements of Gościąż Lake can be interpreted considering the class of plants. The Pinopsida (Class) is characterized by different levels of <sup>14</sup>C in one species but for samples collected at a different time (the same effect is observed in  $\delta^{13}$ C and  $\delta^{18}$ O). In Liliopsida (Class), one can observe two groups of plants: the first group, with higher <sup>14</sup>C concentration contains Carex Paniculata, Carex Rostata, Phragmites Australis, Typha angustifolia, Carex paniculata and the <sup>14</sup>C values show variability from ca 113 to 121 pMC; the second group, with lower <sup>14</sup>C concentration (ca 7 pMC), includes three samples. In the light of the data (Tables 5 and 6, Fig. 13) in Magnoliopsida (Class) which contains Frangula and Betula sp., the variability of <sup>14</sup>C values is from 117 to 119 pMC. The <sup>14</sup>C concentration in *Charophycea* (Class) shows variability from ca 65 to 79 pMC.

The comparison of <sup>14</sup>C and total carbon content in samples from Wigry Lake (Table 4) is presented in **Fig. 14**. Average total carbon content is equal to  $42.0\pm6.8\%$  (n=9). The straight line indicates the weighted mean of carbon content and dashed lines indicate ranges of one standard deviation. The comparison of <sup>14</sup>C and  $\delta^{13}$ C in both fractions (organic and inorganic) is presented in **Fig. 15**. It is observed that the variability of  $\delta^{13}$ C is lower in carbonates than in the organic fraction (plants).

#### 7. SUMMARY

The investigations presented in this study include radiocarbon and stable isotope analyses for recent lacustrine sediments. In Wigry Lake, we observe higher  $\delta^{13}$ C values in plants and associated carbonates under different vegetation conditions than in Gościąż Lake. The difference in  $\delta^{13}$ C values of plants growing under similar conditions can be due to various possible reasons. At this stage of research it is difficult to indicate the most important reason and thus the interpretation of result is not straightforward. Analysis of  $\delta^{13}$ C variation in plants in the whole material and alpha-cellulose shows, in a few cases an isotopic depletion or enrichment. It is also observed that average  $\delta^{13}$ C values in DIC are much lower than in carbonates deposited on plants.

Comparison of  $\delta^{13}$ C and  $\delta^{18}$ O in plants shows that samples can be divided in three groups according to variability and carbon and oxygen isotope composition. Comparison and differences in  $\delta^{13}$ C and  $\delta^{18}$ O within plants in the whole material and in alpha-cellulose shows that a few samples are depleted in heavier isotopes and the other are enriched. It is caused by physiognomy and chemical composition of plants, but at this stage of research it is problematic to explain the reasons.

The <sup>14</sup>C concentration in plants is higher than the activity of radiocarbon in atmosphere before 1950 (before "bomb test"). In 2002, this value was higher by ca 11%. That means that the "bomb effect" is observed in modern annual plants. In Wigry Lake, the highest level of <sup>14</sup>C can be seen in terrestrial plants and lower values in semi submerged and submerged plants. It is caused by the reservoir effect. The "bomb effect" is also observed in the case of Gościąż Lake environment.

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**Fig. 15.** <sup>14</sup>C concentration versus δ<sup>13</sup>C in organic fraction and carbonates. (R<sup>2</sup> - squared of correlation coefficient; the trend lines: straight line - Gościąż Lake and dashed line - Wigry Lake).

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