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Geochemical analysis of the mineral and biogenic deposits from ST3 C3 core was used to reconstruct changes in environmental conditions, mainly changes such as: type and intensity of denudation processes, water level, trophic status, human impact, decomposition of organic matter and origin of organic matter.

Materials and method

So, geochemical analysis involved determining percentage of organic matter (OM), content of terrigenous silica (MM), calcium carbonate ($CaCO_3$), biohpilic elements (C, N, S) and concentration on selected elements (Na, K, Mg, Ca, Fe, Mn, Cu, Zn and Pb). Geochemical procedure was proceeded of few steps (Fig. 1). First, crucibles containing about 5 g wet sediment were kept for 10 hours at -170°C. Subsequently, the crucibles ith the frozen material were placed in the freeze-drier for 24 hours using laboratory lyophilizer Christ Beta 1-8 LD Plus (Photo 1), after which the samples were dried for two hours at 105^{o}C in Memmert oven (Photo 2) and reweighed. Next, about 3 g dried material were placed in the Gallenkamp muffle (Photo 3) combusted at 550°C by 4 hours (loss on ignition, LOI_{550}) and 925°C by 2 hours (LOI_{925}) to content weight. Moreover, the percentage of organic matter and calcium carbonate content was calculated from the difference between sample weights before and after combustion, but the percentage of terrigenous silica was calculated from difference between results of total mass of samples and organic matter and calcium carbonate contents.

The ash obtained after roasting was wet mineralised by dissolving in a mixture of: 8 ml concentrated nitric acid (HNO_3), 2 ml 10% hydrochloric acid (HCl) with the addition of 2 ml perhydrol (H_2O_2). This mineralisation was performer at one cycle in Teflon bombs using a „*Speedwave*" twelve-column ultrasonic mineraliser Berghoff company (Photo 4). The concentration of elements in the obtained solutions was determined by atomic absorption spectrometry (AAS) on a Solaar 969 Unicam company (Photo 5). Operating parameters for AAS instrument were: auxiliary flow: 1.1 l/min; flame typ: air-C_2H_2, measurement time: 4 second, number of measurements: 3. To avoid interactions between the individual elements, a lanthanum solution was used in the concentrations specified by Pinta (1977). The instrumental detection limits (IDL) variable between 0.0016 mg/l for Mn and 0.013 mg/l for Pb and instrumental quantification limits (IQL) various from 0.029 for Mn to 0.10 for Pb (*Instrukcja obsługi…).* The largest of values cones standard used for calibration (4 mg/l for Fe, Mn, Pb, 2.5 mg/l for Cu and 1 mg/l for other metals) take it as linear limits signals-concentration dependence. Finally, the concentrations of most metals were expressed in mg/g d.w. except for Cu, Zn and Pb, which were converted to μg/g d.w.

In addition a total biophilic elements content (in %), such as: carbon (TC), nitrogen (TN) and sulphur (TS) in research samples were determined separately using a VarioMAX analyser (Elementar company; Photo 6) at variable resolution. The weight percentage of the total inorganic carbon (TIC) was drived from the following formula: TIC (%) = 0.27 LOI_{925}.

The total organic carbon (TOC) was calculated by substracting the TIC from the total C (TC). The TOC/N ratio was calculated on a molar basis (Appendix 1). All described analysis were carried out following the procedure for quantifying the content of lithogeochemical elements in lake and peat sediments (*c.f.* Borówka, 1990; Okupny et al., 2020) and reference materials (Sulfadiazine, Agroma Compost – CP1, Metals in sewage sludge – SQC001S, ANALYTIKA Ltd. Solutions/CZ.) were used to control the quality of results.

Results and interpretation

In results, three stages of biogenic accumulation reservoir have been identified after applying the zonation which based on a constrained cluster analysis with PAST version 2.17c software (Hammer et al. 2001). The proportions of analysed component can serve as the basis for reconstruction if environmental changes in the research kettle-hole and its surroundings.

The oldest sediments (**stage I**; depth: 1342-1226 cm) are composed mainly mineral matter (total carbon is very low and does not exceed 1.5%) with an admixture of organic matter came from terrestrial sources because TOC/N index are high (above 25). A twofold increase in the sulphur content (above 4.8% in the sample from 1314 cm depths about 1.5% in the samples from 1254-1242 cm and) indicate rapidly redox conditions in the lake. Moreover, the very high values of Fe/Mn (above 400) seem to indicate low redox conditions at this kettle-hole, which might be associated with high groundwater levels through most Late Weichselian and Early Holocene periods. Although the water levels on this lake show periodic decreases (Ca/Fe ratio increase at the depths: 1318-1290 cm and 1258-1234 cm) in the water table, probably the mainly groundwater-controlled waterlogging of kettle-hole affected the occurrence of relatively high results of Ca (15-23 mg/g d.w.) and Mg (about 7 mg/g d.w.).

Generally the most research samples which deposits were characterized by high content of organic matter (LOI_{550} between 0.25 and 99.8%, average is 80.9%), and $CaCO_3$ is missing (LOI_{925} occur only depth at 1306-1226 cm and range 0.42-25.5%). The total inorganic carbon content are lower and various between 0 and 6.87% and only two samples is higher (depths: 1298 and 1290 cm) than total organic carbon. This results provide a record of chemical denudation in the vicinity of the lake (Na/K ratio rapidly increase from 0.04 to 0.186 and as well as Ca/Mg ratio which variable between 1.09 and 5.11 at the depth: 1318-1290 cm), already at the Late Weichselian period. Moreover described results corresponds with rapidly changes of TOC/N index and indicate of a lacustrine environment still.

The clearly visible accumulation of fine-grained fractions (clay minerals often above 7% or even 9%), indicated by the increasing trend in Na (from 0.06 to 0.68 mg/g d.w.), K (from 1.35 to 6.42 mg/g d.w.) and Mg (from 1.32 to 7.25 mg/g d.w.) concentrations. This interpretation would agree with the increasing values of erosion ratio (such as: Na+K+Mg/Ca), indicating and mineral input from the small but sloping of the catchment (mainly depths: 1334-1318 cm, 1258-1254 cm and 1226 cm). Similar results was noted in the many other kettle-holes in the Europe (Mendyk et al. 2016; Karasiewicz 2019; Okupny et al. 2020; Petera-Zganiacz et al. 2022). At this same time in the nearly Serteya River valley is represented by a still very high content lithophilic elements, such as: K (all results above 8 mg/g d.w.), Na (all results above 0.4 mg/g d.w.) and Mg (all results above 8 mg/g d.w.) in the limnological and sandy silt (see: Płóciennik et al. 2022).

The environmental changes during the deposition of middle part of the research core (**stage II**; depth: 1226-373 cm) corresponds with the stable, but low the molar TOC/N index (mainly below 16, average is 13.6) in the sediments, and indicating a high contribution of lake phytoplankton to production of sedimentary organic matter. Apart trend general increase of TOC and N content from bottom part of the research core to 650 cm indicates gradual increase of productivity, while the short-term geochemical variations maybe caused by changes in the composition of sediment-forming habitats or occurred selected woods in the catchment of lake, which enriches nitrogen in the soil by fixing atmospheric N (Binkley et al., 1994).

The content of lithophilic elements (Na, K and Mg) is general stable with except the lower part of this section (depths: 1226-1168 cm and 666-546 cm). So high denudation processes periods are correlated with Early Holocene (age: 10,111-9,501 cal BC) and Middle Holocene (age: 4,562-2,925 cal BC): the changes in erosion ratio confirm the changes of climate (humidity) and land cover (human impact?) on the catchment area. The occurrence of this periods decrease of Ca/Fe ratio may suggest of increased in the water level. Other signals with very strongly redox conditions (Ca/Fe below 0.4) are documented at the depths: 818-804 cm and 444-404 cm. The stratigraphic variability of Na/K and Ca/mg ratios reflects temporal changes of the type denudation processes occurring in the catchment of the kettle-hole, from mechanical to chemical. Along with a gradual change in the lake sediment composition from mineral deposits to organic sediments enriched in syderophilic elements, such as: Cu, Zn, Fe and S.

The most geochemical proxies show relatively high results of the 804 cm (age: 6,365 BC), so this change seem to be connected with lithology sediments (from clay to detritous gyttja) or change of regional plant communities and possibilities to dissolve of nutrients and mineral from the soils of the catchment. The gradual lowering of the water level in the lake and the transformation to a mire (depth: 436-373 cm) is confirmed by the increase of TOC/N index from 15.1 to 24.7 According Meyers and Teranes (2001) a steady increase in the TOC/N maybe indicates the enhanced delivery of terrestrial organic matter. This core section is associated with the initial sedentation organic matter with decrease of mineral matter to only 4-6%.

The **III stage** (depth: 373-0 cm) is characterized by a decrease the most research elements, with a high content of organic matter (average is 97.8%). A rapid increase TOC/N (from about 25 to 85.9 even) at the depth 154-60 cm indicates a cessation of peat humification or, alternatively, indicates a change in peatforming plants. In the upper part of the research core sulphur content and TOC/N index show decreasing trends (from about 2 to 0.1% and 68.9 to 33.1 respectively), arguing for improved redox conditions within the mire with change of water level and an enhanced decomposition of peat deposits. The Ca/Fe ratio, which is an indicator of water level (see Pleskot et al. 2018) was very low and stable between 934 BC and 1595 AD, reaching a minimum of 502-728 AD. From 1595 AD to the present, not only Ca/Fe ratio, but also Fe/S and Ca/Mg values were clearly higher, and a sharp maximum of c. 1916 AD.

Mineral matter delivered to the kettle-hole from slopes in this phase characterized by a very low concentration of lithophilic elements (Na mainly: 0.1-0.2 mg/g d.w.; K mainly: 0.2-0.4 mg/g d.w. and Mg mainly: 0.2-0.4 mg/g d.w.). Moreover, from c. 1033 AD to the present, the ratio Na/K showed a decreasing trend from 1.4 to 0.24 and suggest the mechanical denudation in the catchment. Towards the top, the peat sediments not became enriched in lithophilic elements, so human activity at the period 1916 AD to present not strongly. This interpretation is supported by high concentrations of trace elements, such as: Cu (maximum: 25.2 µg/g d.w.), Zn (maximum: 127.1 µg/g d.w.) and Pb (maximum: 64.9 µg/g d.w.). Similar results was noted in the Rąbień raised bog (Płaza et al. 2013/2015) and Żabieniec site (Okupny et al. 2021).

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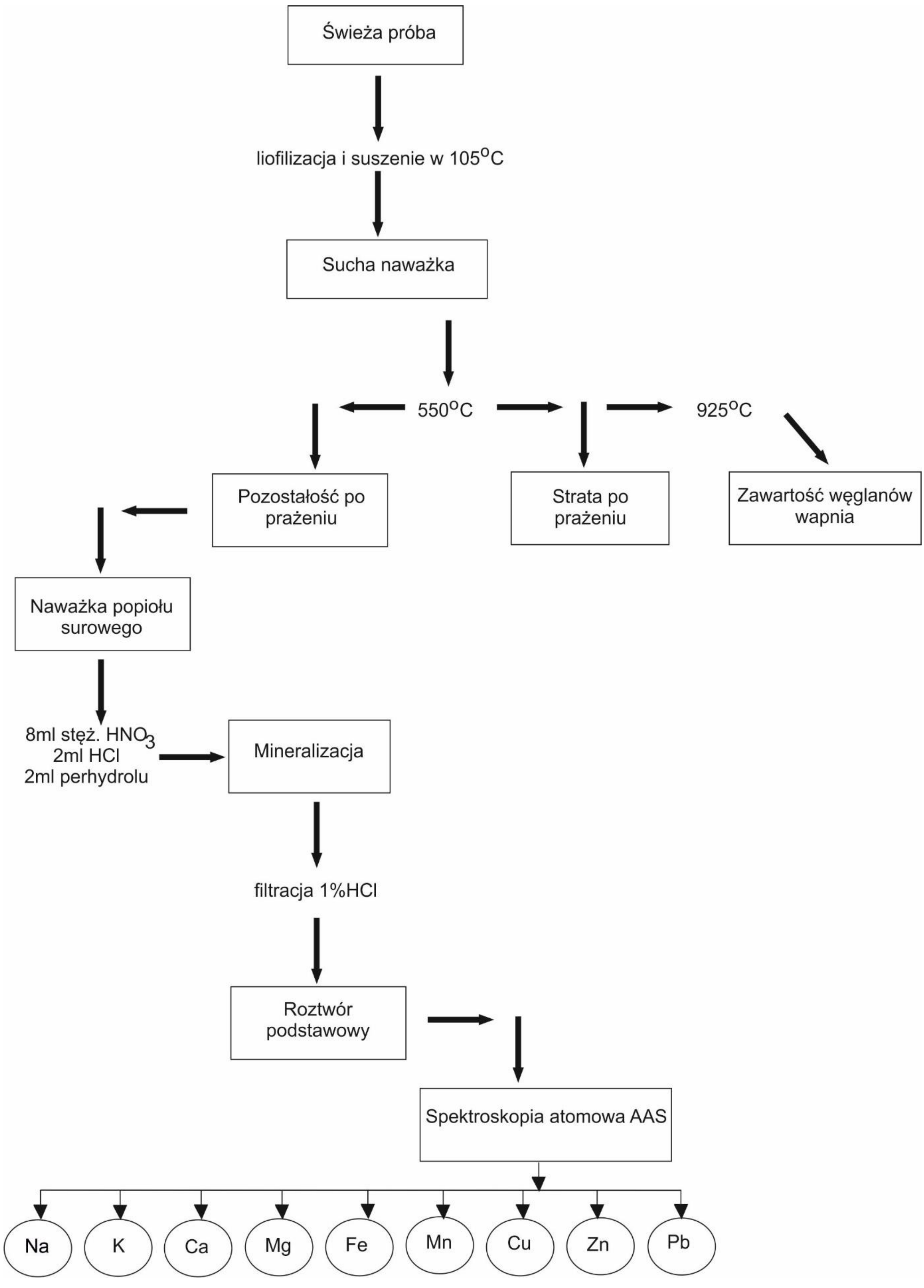

Fig. 1. The procedure of laboratory analysis based on: Borówka (1990)

			
Photo 1. Laboratory lyophilizer for freeze-dried of samples	**Photo 2.** Memmert oven for thermal drying of samples and laboratory equipment	**Photo 3.** Gallenkamp muffle for combusted of samples	**Photo 4.** Twelve-column ultrasonic mineraliser used to prepare solution for further analysis

all photos: Daniel Okupny (2022, 2023)

	
Photo 5. Atomic absorption spectrophotometer (Solaar 969 Unicam company) for measurement content of elements such as: Na, K, Mg, Ca, Fe, Mn, Cu, Zn and Pb	**Photo 6.** VarioMax analyser for measurement content of biophilic elements (C, N and S)

all photos: Daniel Okupny (2022, 2023)