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RADIOCARBON DATING OF PEAT PROFILE WITH METALLURGY INDUSTRY EVIDENCE

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Abstract: In this work an age model for a peat core from the site near Żyglin, based on ^{14}C is presented. The investigated profile is marked with some possible evidence of early human activity in this region. The earliest metallurgy industry is expected to correspond with charcoal production and the recent increase of metal content in this profile. In this work the Quantulus 1220™ recently purchased was used for ^{14}C dating with liquid scintillation counting (LSC) technique. Therefore results of calibration, tests and verification with use of samples from inter-comparison programs (VIRI, FIRI) are also presented.

Keywords: ^{14}C dating, LSC, peat, Poland, Żyglin

1. INTRODUCTION

In the Upper Silesia (the South of Poland) there are a few archaeological sites with evidence of early human activity and therefore they are very valuable in archaeological investigations. Probably one of the most important type are peat-bogs. Growing peat-bogs recorded human activity as change of Pb, Cu, Zn and other elements introduced by metallurgy industry.

First investigations showed that metallurgy industry had a large impact from 9th century (AD) until the Second World War. Those investigations were carried out and described by Chróst *et al.* (2007 and 2008). It was shown that a large amount of charcoal and metals is deposited in peat. This is known to be typical for early metallurgy based on ores of Fe_2O_3 and $Fe_2O_3{\bullet}nH_2O$ (Godfrey-Smith and Casey, 2003; Rapp, 2009). Moreover, charcoal, Pb, Zn, Cu as well as some other metals are very often considered as immobile in peat (Vile *et al.*, 1999, Ali *et al.*, 2008). This ensures suitability of profiling Pb, Zn and Cu in peat profiles to trace metallurgical activity. Investigations were made by Laboratory for Ecological Research, Measurement and Expertise ”EKOPOMIAR” Leszek Chróst from Gliwice and Environmental Protection Section of Society of Friends of Tarnogórska Land from Tarnowskie Góry. Chemical analyses of concentration of metals were made by the Center of Environmental Control and Survey from Katowice.

One of investigated peat areas (**Fig. 1**) near Żyglin was marked with the very large amount of charcoal, even in comparison with other peat profiles from this area. The first radiocarbon dating showed that peat core covers the Iron and Bronze Age.

Independent investigations were started by unit from the Center of Environmental Control and Survey (Greger and Składowski, 2009). The Gliwice Radiocarbon Laboratory began its own project of creating the age-depth model which will bond all the events to absolute time scale.

2. ŻYGLIN SITE

The material was collected near Żyglin (**Fig. 1**). The coordinates of the taken core are N 50°28’56.20’’, E 18°59’12.19’’, 249 m AMSL. The fen has a triangular shape and was devastated by drainage twice: in the interwar period and in the 1980s. The peat spans over the area of 2 ha and is situated near the drainage basin of the Brynica river. Thanks to 20 cm of sand layer covering the surface, the fen was preserved for a long period of time. Until 2009, 8 profiles were investigated from this fen. Profiles marked by numbers 2 and 3, dated in this paper by radiocarbon method, come from the same part where the largest thickness of fen-bed was found. The previous dating of fen bedrock layer in profile 1, with the use of

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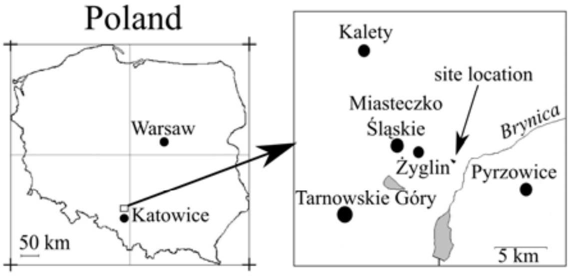

Fig. 1. *Location of peat-bog near Żyglin.*

conventional ^{14}C method suggested continuity of peat growth in the last 12,000 years.

In the upper part of the core a large amount of charcoal was found. Four samples of carbonized wood from this fen were dated in Poznan Radiocarbon Laboratory with the use of AMS method (financed by Municipal Office of Miasteczko Śląskie and Zinc Works "Miasteczko Śląskie"). Final conventional age results were calibrated using OxCal v4.1.3 (Bronk Ramsey, 2009) and IntCal04 Northern Hemisphere calibration curve (Reimer *et al.,* 2004).

It was showed that charcoal pollution process took place from around 2500 BC (**Table 1**). A hypothesis was put forward, that such a long period of charcoal production was connected with igneously gentrified ochre (hematite), which occurs in Żyglin region and in subsequent period with siderurgy and for smaller scale with metallurgy of lead and silver. Copper content measurements show unexpected triple increase of this metal on the depth from 61 to 62 cm, compared to other parts of the core (Greger and Skałdowski, 2009). The large amount of charcoal in this profile is found to the depth of 64 cm. In summary, it can be said that results obtained from measurements done so far suggest the existence of metallurgy industry (copper, lead, silver and iron) in the last 4000 years. This roughly matches know human settlement and activities in this part of Europe (Bellwood, 2004; Cavalli-Sforza *et al.,* 1994). Initial chemical analysis also showed, that in the earliest period ochre (hematite) was igneously gentrified.

3. ^{14}C DATING

Sampling

The peat core was taken near the drainage ditch after removing approximately 1.5 m of peat up to a place not affected by human activity. The total length of the core was 130 cm. The uppermost 20 cm-section of the core was composed mainly of the sand, the remaining 110 cm was composed of peat. The core was cut into slices 1 cm each in the upper part (20-90 cm) and in the lower part (90-130 cm) each 2.5 cm. In order to avoid enriching material with modern ^{14}C the samples were stored in the dark room in the fridge until further procedures were undertaken.

Chemical pre-treatment of the samples and conversion to benzene

Samples were treated with the standard procedure Acid-Alkali-Acid (Cook *et al.,* 1998) to remove humic acids, chitin, fungal products, etc. Next, they were pyrolised in a reactor at 650°C and lithium carbide was produced at 800°C. Subsequently, the lithium carbide was flooded with demineralised water to obtain acetylene (C_2H_2). In the final stage, benzene (C_6H_6) was obtained by the catalytic trimerization of acetylene on vanadium catalyst. Benzene line was designed and produced by Skripkin from Kiev. More detailed description of vacuum rig for benzene synthesis can be found in Pawlyta *et al.* (1998). The benzene production samples were stored for over one month to let all ^{222}Rn and daughter isotopes to decay.

Calibration of Quantulus and ^{14}C measurement

In 2008, the new Quantulus 1220™ was installed in Gliwice Radiocarbon Laboratory. Before using for routine measurements, the new Quantulus 1220™ required calibration and a verification test. We performed calibration according to Pawlyta *et al.* 1998 for 2 ml geometry samples since we were very confident with our earlier results.

The pulse amplitude comparator allows to reduce the background by rejecting events giving vastly different pulses ratio in two photo multiplier tubes. The PAC level is allowing to adjust such a ratio. As a result of calibration the optimal value of PAC was chosen where following function reaches the minimum value:

$$O(\mathrm{PAC}) = \frac{B(\mathrm{PAC})}{E_r^2(\mathrm{PAC})}, \tag{3.1}$$

where: E_r – relative counting efficiency, B – background counting rate. E_r and B are functions of PAC. In **Eq. 3.1**, E_r in is calculated according to:

$$E_r(\mathrm{PAC}) = \frac{S_{0\mathrm{u}\max}}{S_{0\mathrm{u}}(\mathrm{PAC})}, \tag{3.2}$$

where: S_0 is modern standard counting rate calculated according to Polach and Stuiver (1977), $S_{0\max}$ responds to the highest counting rate of modern standard and

Table 1. *Results of radiocarbon dating of charcoal.*

Charcoal sample No.	Conventional age (BP)	Calibrated age range 68.2%	Calibrated age range 95.4%
Poz-26362	3890 ± 35	2465-2340 BC (68.2%)	2475-2285 BC (93.8%) 2250-2235 BC (1.6%)
Poz-26979	3920 ± 35	2475-2400 BC (45.3%) 2385-2345 BC (22.9%)	2550-2535 BC (1.2%) 2490-2290 BC (94.2%)

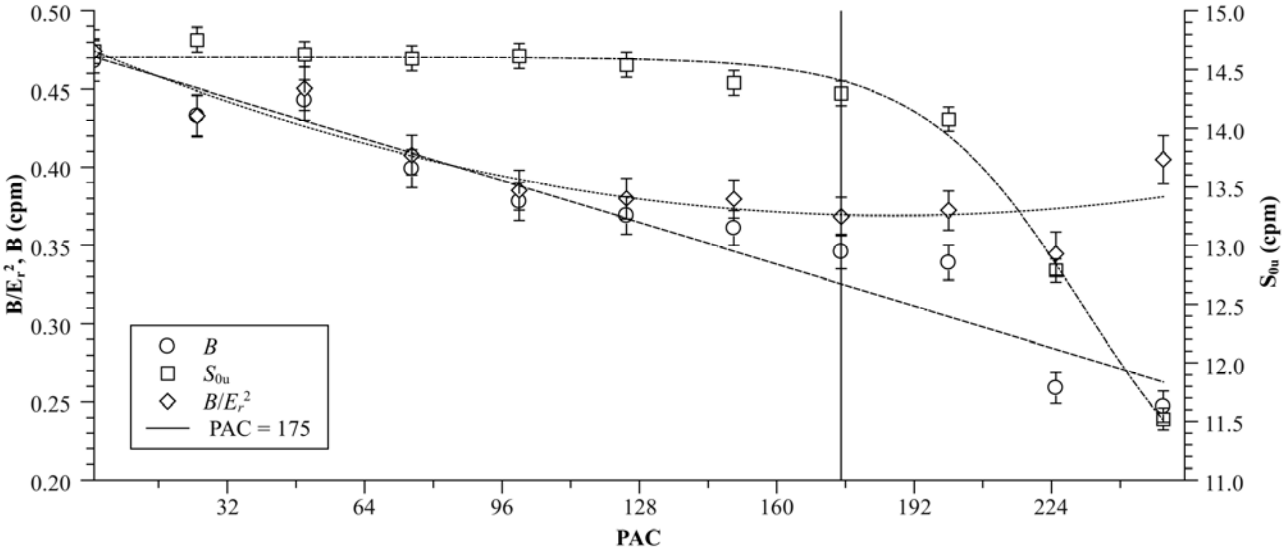

Fig. 2. *B, S_{0u} and B/E_r^2 as PAC function. The optimal PAC value is 175.*

S_0(PAC) modern standard counting rate as a function of PAC. The u refers to values that are not corrected according to quenching effect. We set the PAC level for 175 (**Fig. 2**).

The factor of merit (FOM) is defined as:

$$\mathrm{FOM}(LD,HD)=\frac{S_{0\mathrm{u}}(LD,HD)}{\sqrt{B(LD,HD)}}. \tag{3.3}$$

Routinely we use a fixed counting window (**Fig. 4**). The lower band of ^{14}C window is just above tritium spectrum to avoid its low energy beta radiation from the water used in benzene synthesis. The upper band is almost at the end of ^{14}C spectrum. The window that spans from channel 291 to 580 was chosen. It can be seen (**Fig. 3)** that the position of ^{14}C window, corresponds to almost

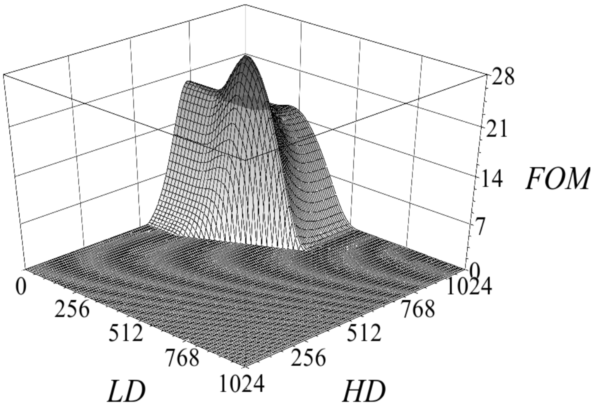

Fig. 3. *FOM as a function of lower (LD) and higher (HD) band of ^{14}C window.*

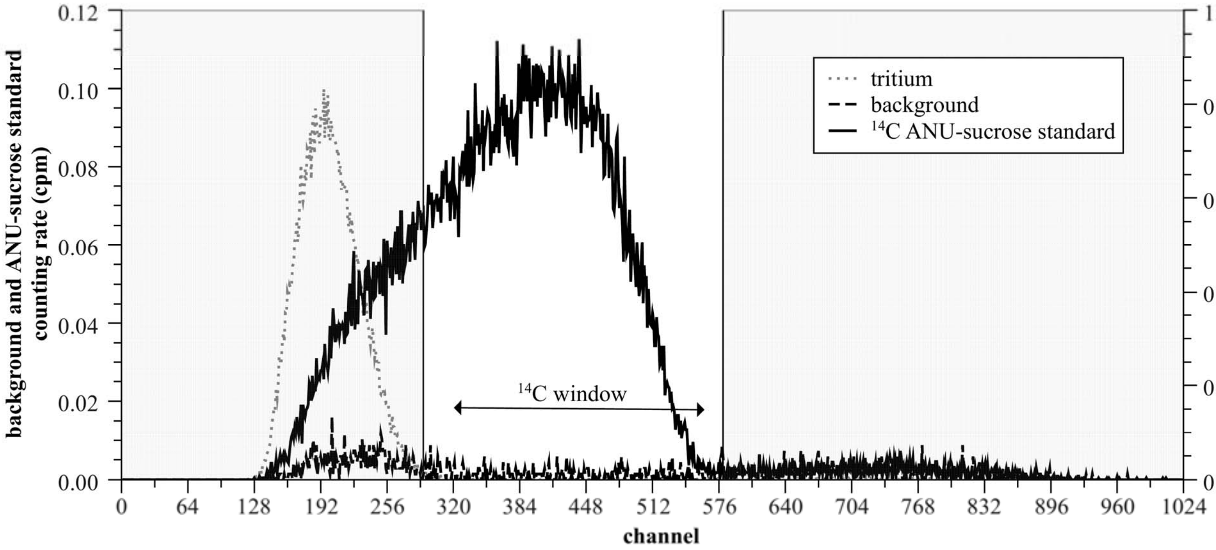

Fig. 4. *Tritium, ^{14}C and background spectra with marked ^{14}C window.*

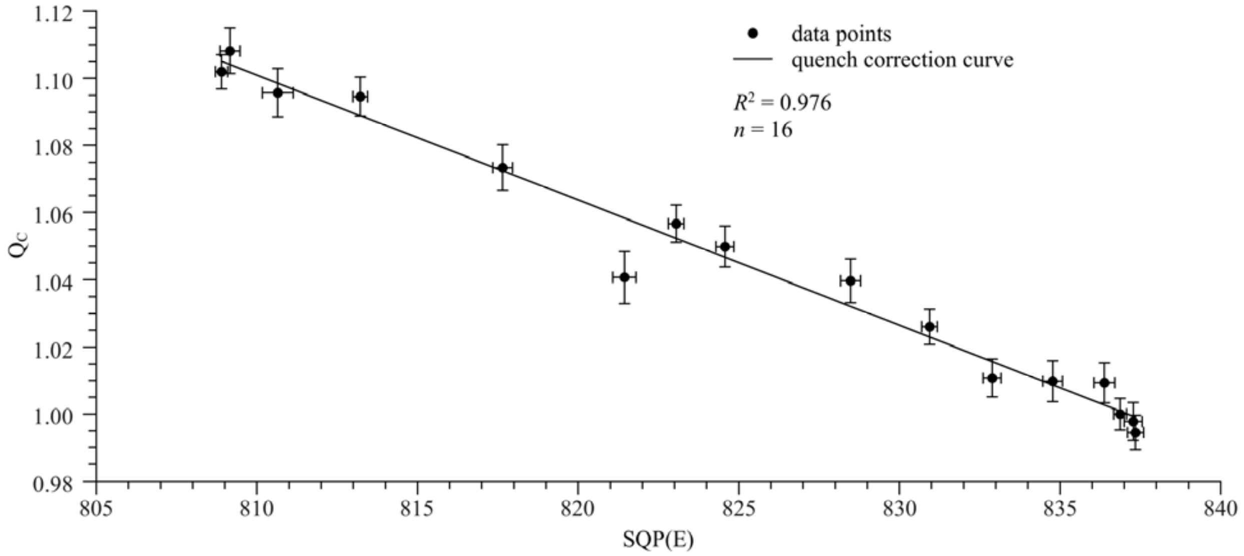

Fig. 5. *Quench correction vs. quenching indicator SQP(E).*

maximum of FOM surface. This will benefit when old or diluted samples are measured. In the next step we build up a quench correction curve (Q_c) by quenching with acetone ANU-sucrose (**Fig. 5**). ANU-sucrose is a secondary standard proposed by Polach and Krueger (1972). The quench correction is defined as

$$Q_C(\mathrm{SQP}(\mathrm{E})) = \frac{1}{E_r(\mathrm{SQP}(\mathrm{E}))}, \tag{3.4}$$

where E_r(SQP(E)) is relative efficiency as a function of SQP(E).

The explanation of spectral quench parameter of external standard (SQP(E)) of Quatulus 1220™ can be found for example in PerkinElmer® instrument manual (2005). Obtained SQP(E) range (808-837) corresponds to the range of different purities of typical samples.

The Quantulus 1220™ is known for its stability and reproducibility. For ^{14}C data evaluation we use a wide range of activity standards and backgrounds. **Fig. 6** shows result of the series of background measurements that were used and **Fig. 7** shows counting rate of modern biosphere standards measurements.

The results presented in **Figs. 6** and **7** prove that measurements carried out with use of new Quantulus 1220™ can be considered stable and reproducible. The basic parameters of Quantulus 1220™ are listed in **Table 2**.

In order to test the reliability of new Quantulus 1220™ we used available samples from International Radiocarbon Inter-comparison (VIRI, FIRI). Consensus VIRI values were reported by Scott in 2009 at the Radiocarbon Conference. The FIRI values were reported by Boaretto *et al.* (2002). The results are provided in **Table 3**.

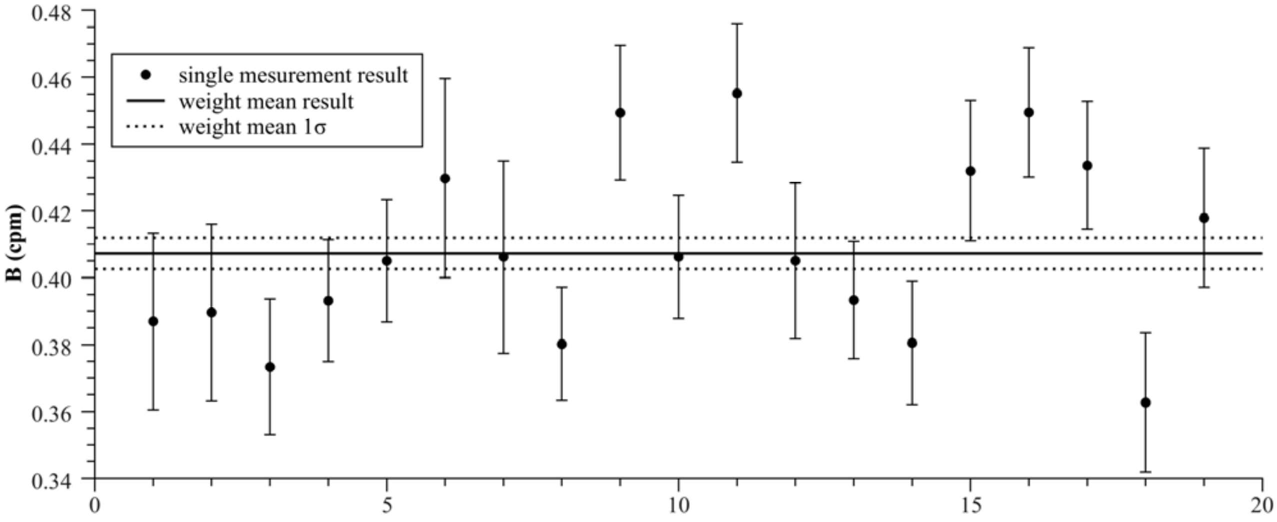

Fig. 6. *Background counting rate stability and reproducibility with 1σ uncertainty for single measurement. 2-3 day measurements spanned over 8 months.*

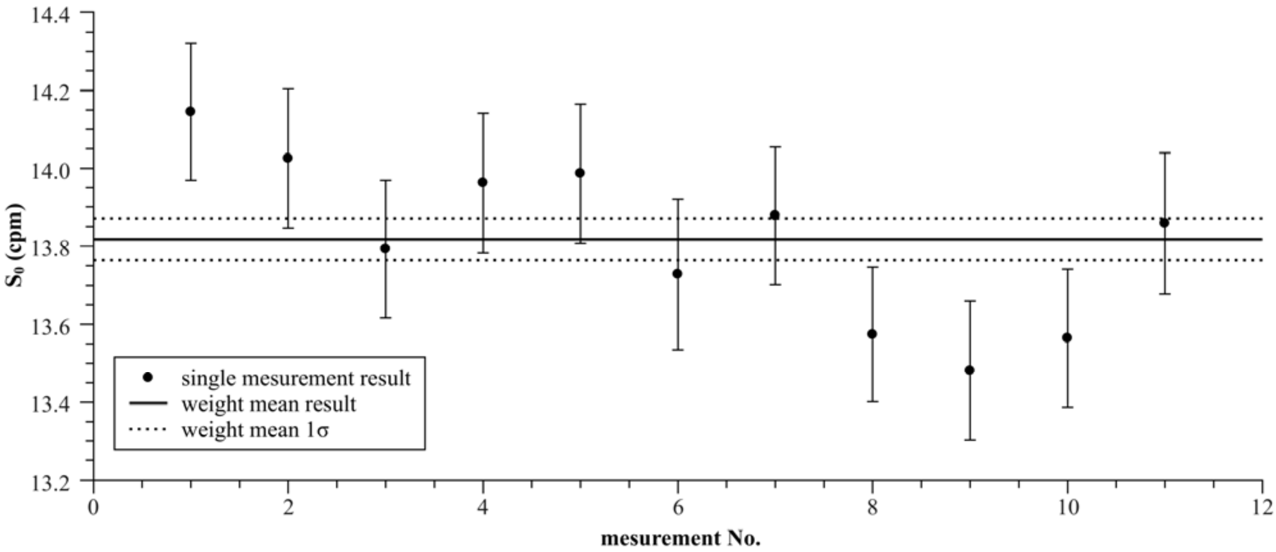

Fig. 7. *Standard stability and reproducibility with 1σ uncertainty for single measurement points. 2-3 day measurements spanned over 8 months.*

4. DATING RESULTS AND AGE-DEPTH MODEL

A number of 17 peat samples were taken from Żyglin 3 core for conventional radiocarbon dating in Gliwice Radiocarbon Laboratory. The obtained dates were calibrated using OxCal v4.1.3 (Bronk Ramsey, 2009) and IntCal04 Northern Hemisphere calibration curve (Reimer *et al.,* 2004). An age model was constructed from this data set on the basis on P_Sequence(0.1) (Bronk Ramsey, 2008). There were a lot of events that influenced this peat during last 14 kyr, taking into account that peat is very compressed (ca. 0.07 mm·yr^{-1}), k = 0.1 parameter is allowing for a number of changes. The similar peat age-depth model of a comparable time span was reported by Lamentowicz *et al.* (2009). **Fig. 8** and **Table 4** present the results of calibration and model.

5. SUMMARY AND CONCLUSIONS

The obtained age-depth model is characterised by good agreement of all the data points, as no inversions of dates were observed. Modelled distributions fit well to the model to a priori information and agreement parameter of model is A_{model} = 73%. One of the samples, Żyglin 3/28-29 seems to be out of age-depth model (**Fig. 8**) but the agreement (51.6%) is not low enough to determine if the sample is outlier. Much more precise and complex age-depth model is being developed.

Further investigations will include precise determination of time periods in which metals were smelted by means of radiocarbon and chemical investigations. It can be done by seeking for presence of those particular metals in dated peat levels. The origin of metals would be a very valuable information and in some cases it can be obtained by analyses of lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) ratios. The measurements are currently in progress in frame of the cooperation between Silesian University of Technology (Poland) and University of Liege (Belgium).

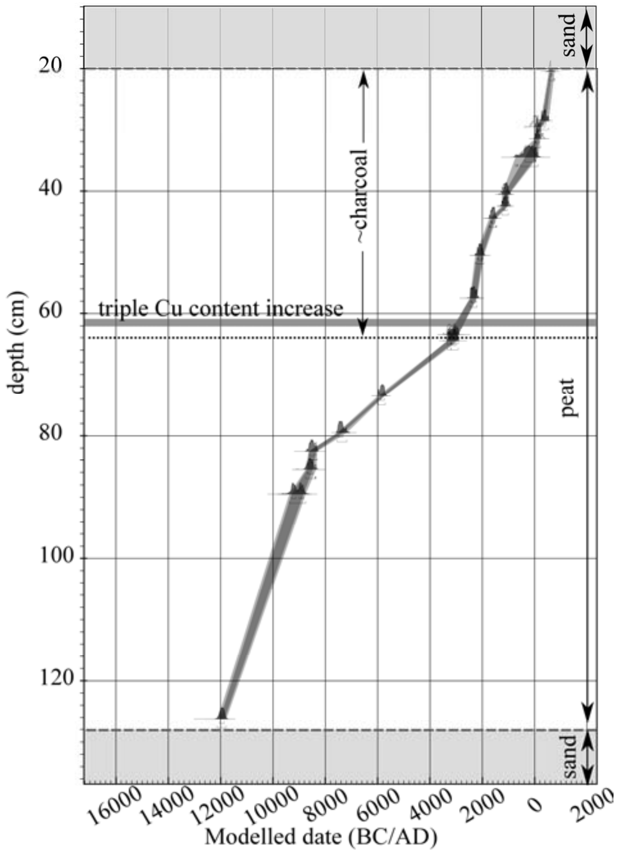

Fig. 8. *Age depth model of investigated profile with approximately marked levels of Cu increase and section of high charcoal content.*

Table 2. *Basic parameters of Quantulus 1220™.*

Geometry	2 ml
S_0 (cpm)	13.817 ± 0.054
B (cpm)	0.4072 ± 0.0047
FOM (cpm$^{0.5}$)	21.7
$T_{\max}$* (BP)	44100

* - for 1000 min measuring time

Table 3. *Quantulus 1220™ calibration verification with results from inter-comparison programs.*

Sample name	Unit	Quantulus 1220™		Consensus values	
		Value	1σ	Value	1σ
VIRI B	(BP)	2825	65	2820	4
VIRI C	(pMC)	107.15	0.58	110.7	0.04
VIRI D	(BP)	2895	65	2836	4
FIRI C	(BP)	17740	190	18176	10.5
FIRI F	(BP)	4495	115	4508	3
FIRI I	(BP)	4200	160	4485	3
FIRI J	(pMC)	108.33	1.5	110.7	0.04

Table 4. *Conventional radiocarbon age and modelled age range.*

Sample name	Depth (cm)	Conventional age (BP)	Modelled age range 68.2%	Modelled age range 95.4 %	Agreement (%)
Żyglin 3/125-127.5 cm	125-127.5	12040 ± 80	12035-11850 BC (68.2%)	12165-11775 BC (95.4%)	99.5
Żyglin 3/89-90 cm	89-90	9740 ± 110	9290-9130 BC (33.5%) 9005-8835 BC (34.8%)	9375-8750 BC (95.4%)	91.2
Żyglin 3/85-86 cm	85-86	9320 ± 80	8695-8680 BC (3.4%) 8650-8475 BC (64.8%)	8755-8350 BC (95.4%)	109.7
Żyglin 3/82-83 cm	82-83	9265 ± 70	8615-8435 BC (66.9%) 8365-8355 BC (1.3%)	8640-8305 BC (95.4%)	104.9
Żyglin 3/79-80 cm	79-80	8340 ± 75	7515-7330 BC (68.2%)	7545-7180 BC (95.4%)	100.9
Żyglin 3/73-74 cm	73-74	6945 ± 70	5895-5745 BC (68.2%)	5985-5715 BC (95.4%)	99.8
Żyglin 3/64-65 cm	64-65	4435 ± 65	3330-3220 BC (28.2%) 3180-3160 BC (3.4%) 3120-3010 BC (35.2%) 2980-2970 BC (1.4%)	3340-3205 BC (32.3%) 3195-2925 BC (63.1%)	102.9
Żyglin 3/63-64 cm	63-64	4445 ± 90	3310-3295 BC (2.2%) 3285-3230 BC (10.9%) 3170-3160 BC (1.0%) 3120-2925 BC (54.0%)	3330-3205 BC (25.7%) 3195-2915 BC (69.7%)	105.1
Żyglin 3/57-58 cm	57-58	3865 ± 50	2455-2415 BC (13.7%) 2410-2285 BC (51.6%) 2250-2235 BC (2.9%)	2470-2195 BC (95.4%)	99.0
Żyglin 3/50-51 cm	50-51	3695 ± 50	2195-2175 BC (6.8%) 2145-2020 BC (59.3%) 1995-1980 BC (2.1%)	2275-2255 BC (1.3%) 2210-1935 BC (94.1%)	91.5
Żyglin 3/44-45 cm	44-45	3315 ± 55	1665-1650 BC (5.0%) 1645-1520 BC (63.2%)	1740-1705 BC (4.3%) 1700-1490 BC (89.1%) 1480-1455 BC (2.0%)	99.8
Żyglin 3/42-43 cm	42-43	2910 ± 50	1210-1140 BC (27.4%) 1135-1050 BC (40.8%)	1265-1010 BC (95.4%)	104.9
Żyglin 3/40-41 cm	40-41	2915 ± 55	1190-1175 BC (3.4%) 1165-1140 BC (7.1%) 1135-1020 BC (57.7%)	1260-1225 BC (3.3%) 1220-975 BC (92.1%)	111.3
Żyglin 3/34-35 cm	34-35	2205 ± 145	370-40 BC (59.7%) 15BC-5 AD (2.8%) 10-25 AD (2.2%) 40-65 AD (3.5%)	735-690 BC (1.4%) 665-650 BC (0.3%) 550BC-135 AD (93.7%)	91.1
Żyglin 3/31-32 cm	31-32	1830 ± 55	30-40 AD (2.0%) 50-145 AD (60.8%) 155-170 AD (3.6%) 195-205 AD (1.8%)	10-235 AD (95.4%)	76.9
Żyglin 3/29-30 cm	29-30	1990 ± 65	55-140 AD (53.0%) 160-170 AD (2.7%) 185-220 AD (12.5%)	15-240 AD (95.4%)	51.6
Żyglin 3/28-29 cm	28-29	1660 ± 50	255-290 AD (13.5%) 325-435 AD (54.7%)	240-535 AD (95.4%)	95.3
Żyglin 3/20-21 cm	20-21	1410 ± 55	585-665 AD (68.2%)	535-715 AD (93.8%) 745-770 AD (1.6%)	98.9

Due to the conditions and sand covering the fen the peat has not decomposed for over 14 kyr which gives a perfect opportunity to investigate early human activity and climate changes in Silesia region. On the other hand, the high compaction is main difficulty, and great care is need while bonding events to the time scale.

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REFERENCES

Ali AA, Ghaleb B, Garneau M, Asnong H and Loisel J, 2008. Recent peat accumulation rates in minerotrophic peatlands of the Bay James region, Eastern Canada, inferred by ^{210}Pb and ^{137}Cs radiometric techniques. *Applied Radiation and Isotopes* 66 (10) 1350–1358, DOI 10.1016/j.apradiso.2008.02.091.

Bellwood PS, 2004. *First Farmers: The Origins of Agricultural Societies*. Padstow, Blackwell Publishers: 384pp.

Boaretto E, Bryant C, Carmi I, Cook G, Gulliksen S, Harkness D, Heinemeier J, McClure J, McGee E, Naysmith P, Possnert G, Scott M, van der Plicht H and van Strydonck M, 2002. Summary findings of the fourth international radiocarbon intercomparison (FIRI)(1998–2001) *Journal of Quaternary Science* 17(7): 633–637, DOI: 10.1002/jqs.702.

Bronk Ramsey C, 2008. Deposition models for chronological records. *Quaternary Science Reviews* 27(1-2): 42-60, DOI 10.1016/j.quascirev.2007.01.019.

Bronk Ramsey C, 2009. Bayesian analysis of radiocarbon dates. *Radiocarbon* 51(1): 337-360.

Cavalli-Sforza LL, Menozzi P, Piazza A, 1994. *The History and Geography of Human Genes*. New Jersey, Princeton University Press: 1088pp.

Chróst L, Kandzia M and Wasielewski R, 2007. Sprawozdanie końcowe z wykonania zadania publicznego “Określenia intensywności dawnej produkcji srebra i ołowiu w rejonie Tarnowskich Gór w oparciu o pomiary depozycji ołowiu w torfowiskach” (Final report on the Estimation of the intesity of the early Silver and Lead production in the region of Tarnowskie Góry, Poland, based on the deposition of Lead recorded in peat bogs). Project on Public Procurement. Wydział Kultury Urzędu Marszałkowskiego Woj. Śląskiego (Katowice, Poland) i Stowarzyszenie Miłośników Ziemi Tarnogórskiej (Tarnowskie Góry, Poland): 52pp (in Polish).

Chróst L, Kandzia M and Wasielewski R, 2008. Sprawozdanie końcowe z wykonania zadania publicznego „Określenie usytuowania w rejonie Tarnowskich Gór ośrodków wczesnośredniowiecznego hutnictwa ołowiu i srebra metodą pomiarów lokalnego skażenia torfowisk i gleb ołowiem” (Final report on the Localization of the early medieval Silver-Lead smelting centers in the area of Tarnowskie Gory, Poland, based on the determination of the Lead contamination of soil and peat. Project on Public Procurement.) Wydział Kultury Urzędu Marszałkowskiego Woj. Śląskiego (Katowice, Poland) i Stowarzyszenie Miłośników Ziemi Tarnogórskiej (Tarnowskie Góry, Poland): 38pp (in Polish).

Cook GT, Dugmore AJ, Shore JS, 1998. The influence of pretreatment on humic acid yield and ^{14}C age of carex peat. *Radiocarbon* 40(1): 21-27.

Godfrey-Smith DI Casey JL, 2003. Direct thermoluminescence chronology for Early Iron Age smelting technology on the Gambaga Escarpment, Ghana. *Journal of Archaeological Science* 30:1037–1050, DOI 10.1016/S0305-4403(02)00292-3.

Greger J and Składowski M, 2009. Determination of Copper in acidic peat extracts from the selected layers of the Żyglin peat bog profile acquired in 2008. Report from Ośrodek Badań i Kontroli Środowiska (Katowice, Poland) 1pp (in Polish).

Lamentowicz M, Balwierz Z, Forysiak J, Płóciennik M, Kittel P, Kloss M, Twardy J, Żurek S and Pawlyta J, 2009. Multiproxy study of anthropogenic and climatic changes in the last two millennia from a small mire in central Poland. *Hydrobiologia* 631: 213–230, DOI 10.1007/s10750-009-9812-y.

Pawlyta J, Pazdur A, Rakowski A, Miller B F and Harkness D D, 1998. Commissioning of Quantulus 1220™ liquid scintillation beta spectrometer for measuring ^{14}C and ^{3}H at natural abundance levels. *Radiocarbon* 40(1): 201-209.

PerkinElmer®, 2005. Wallac 1220 Quantulus™ Ultra Low Level Liquid Scintillation Spectrometer. Instrument manual, 1220-931-08.

Polach, HA and Krueger, HA, 1972. Isotopic fractionation of NBS oxalic acid and ANU-sucrose radiocarbon dating standards: international conference on radiocarbon dating, 8th, Wellington, New Zealand, Proc, p 718-724.

Rapp GR, 2009. *Archaeomineralogy*. Berlin, Springer: 348pp, DOI 10.1007/978-3-540-78594-1.

Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Bertrand C, Blackwell PG, Buck CE, Burr G, Cutler KB, Damon PE, Edwards RL, Fairbanks RG, Friedrich M, Guilderson TP, Hughen KA, Kromer B, McCormac FG, Manning S, Bronk Ramsey C, Reimer RW, Remmele S, Southon JR, Stuiver M, Talamo S, Taylor FW, van der Plicht J, and Weyhenmeyer CE. 2004. IntCal04 terrestrial radiocarbon age calibration, 0-26 cal kyr BP. *Radiocarbon* 46(3): 1029-1058.

Scott M, 2009. A first summary of the consensus values for all the VIRI samples. Results were reported at the Radiocarbon conference in Hawaii (detailed report is being prepared for publication. Consensus values available at WEB site: <http://www.radiocarbon.org/>. Accessed 2009 November 11.

Stuiver M, Polach HA 1977. Discussion reporting of C-14 data. *Radiocarbon* 19(3): 355-363.

Vile1 MA, Kelman Wieder R and Novák M, 1999. Mobility of Pb in Sphagnum-derived peat. *Biogeochemistry* 45: 35–52, DOI 10.1023/A:1006085410886.