

The environmental impact of cultural change: palynological and quantitative land cover reconstructions for the last two millennia in northern Poland

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1 **Evidence for the onset of mining activities during the 13th century in Poland using lead**
2 **isotopes from lake sediment cores**

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10

11 **ABSTRACT**

12 Efforts to study how human activities have influenced the environment since the end of the
13 Roman period to present day are lacking for North Central Europe. Here, we present new lead (Pb)
14 isotope data determined from two sediment cores collected from ancient lakes spanning the last
15 1,500 years, located in the Kuyavian-Pomeranian Voivodeship, Poland. Study sites at Radzyń
16 Chełmiński and Rywałd were used to differentiate Pb sources. **Radzyń Chełmiński is located in**
17 **the vicinity of a late Medieval Teutonic Order castle and town, while Rywałd is situated within a**
18 **relatively pristine area until the 19th century when it became used for agricultural purpose.** Core
19 samples were analyzed for Pb concentration and isotopes (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb). Bayesian modelling
20 was used to isolate the anthropogenic signal at each site over time.

21 For both sites, Pb enrichment factors relative to titanium (Ti) and upper continental crust
22 values range from 13 to 159. Lead isotopic ratios range from background, pre-anthropogenic local
23 values ($^{206}\text{Pb}/^{207}\text{Pb} = 1.31 \pm 0.03\%$, $^{208}\text{Pb}/^{206}\text{Pb} = 1.97 \pm 0.04\%$) to anthropogenic values (SW
24 Poland coal, ore, slag $^{206}\text{Pb}/^{207}\text{Pb} = 1.17 \pm 0.01\%$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.09 \pm 0.01\%$). Modeled
25 anthropogenic contribution varies greatly over time, ranging from 14 to 100%. At Radzyń
26 Chełmiński, modeled anthropogenic Pb contribution and measured Pb concentration follow
27 similar trends. However, at Rywałd, from around A.D.1000 to A.D. 1400 these profiles diverge
28 significantly. Our new insights highlight different sources of Pb from the 12th century to present
29 day: (1) short range agricultural activities from the town, and (2) long range mining activities.
30 Additionally, prior to the 12th century, our data suggest continental anthropogenic activity possibly
31 favored by a warmer climate.

32

33 **KEYWORDS**

34 Lead – Isotopes – Sediments – Anthropogenic – Sources – Medieval

35

36 **1. INTRODUCTION**

37 Lead (Pb) is a toxic, non-essential, trace element particularly useful for tracking
38 anthropogenic input in environmental archives (e.g. Lanphear et al., 2005). Using Pb isotopes, we
39 can differentiate between anthropogenic (industrial and mining activities, coal and fuel burning;
40 e.g. Cheng and Hu, 2010) and natural sources (i.e. natural weathering processes) that release Pb
41 into the environment (Grousset et al., 1994; Thevenon et al., 2011; Zohar et al., 2014); and as a

42 result, hypothesize on the timing and locations of past human activities (Fagel et al., 2014; Hosono
43 et al., 2016; Zohar et al., 2014).

44 Three radioisotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) are commonly measured for this type of study
45 (Alfonso et al., 2001; Komarek et al., 2008; Reimann et al., 2012). Due to the durations of their
46 half-lives, these isotopes are considered meta-stable in geologically recent sediment (e.g. Russell
47 and Farquhar, 1960). There are no known environmental or industrial processes that fractionate
48 Pb isotopes, and thus the isotopic composition of Pb is affected by Pb source and geologic location
49 (Cheng and Hu, 2010; Doe, 1970; Flegal and Smith, 1995). Additionally, Pb is relatively stable
50 within the sediment column and not readily susceptible to remobilization by early diagenetic
51 processes or biological activities (Audry et al., 2011; Gallon et al., 2004; Harlavan, 1998; Huerta-
52 Diaz, 1998; McIntyre and Gueguen, 2013; Schultz et al., 1987; Tessier et al., 1996). By analyzing
53 ratios of these three isotopes: $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, it is possible to assess how source
54 contributions of Pb have changed over time for a given location (Baron et al., 2006; Harlavan et
55 al., 2010; Zohar et al., 2014).

56 Within the environment, Pb isotope ratios may be influenced by local, regional, or global
57 sources (e.g. Choi et al., 2007, Martinez Cortizas et al., 2002, 2016, Mil-Homens et al., 2013,
58 2017). For example, In the Iberian Peninsula a number of studies have used Pb isotope ratios to
59 document evidence of regional metallurgy and mining from the Chalcolithic (~3000 BC) to
60 modern period (last 200 years; Martinez Cortizas et al., 2002, 2016, Mil-Homens et al., 2013). In
61 marine sediment within the Portuguese Margin, Pb isotope ratios were also able to record Roman
62 and modern mining activities from the adjacent Iberian region (Mil-Homens et al., 2017, (Include
63 examples from above refs.) Global signatures from atmospheric transport and deposition of Pb,
64 such as Saharan dust storms, and leaded gasoline emissions in modern times, has also been

65 documented (e.g. Bi et al., 2017, Mil-Homens et al., 2017, Shotyk et al., 1998). For this study,
66 regional sources are defined as mining of coal ore, smelting, and leaded gasoline exhaust.
67 Historical mining activities 300 to 500 km to the southwest of the study site may have introduced
68 Pb to the atmosphere, allowing for transport downwind to the study site. This Pb transported over
69 long range is deposited, via association with sinking particles, in lake and peat sediments (e.g.
70 Novak et al., 2003). Local sources, on the scale of kilometers or less, can also contribute to Pb
71 enrichments and/or changes in the Pb isotope ratios in sediments. They include enhanced
72 weathering and erosion of the surrounding landscape due to agricultural activities, building
73 development, metalwork, and domestic coal burning.

74 Regional patterns of Pb transport are of particular interest in Poland due to Poland's unique
75 climatic signal in comparison to the rest of Europe, which is sensitive to both oceanic and
76 continental influences (e.g. Zamoyski, 1987). Specifically, the Medieval Warm Period (MWP)
77 ended in Poland earlier than the rest of Europe (Medieval Warm Period: MWP; A.D. 800 to 1300;
78 e.g. De Vleeschouwer et al., 2009a). The portion of the MWP that influenced Poland is known as
79 the Climatic Optimum in Poland (COP, A.D. 800 to 1150; e.g. Pluskowski, 2013). These climatic
80 patterns may have played two non-mutually exclusive impacts on anthropogenic Pb contributions:
81 directly by impacting efficiency of atmospheric Pb long range transport from mining regions, and
82 indirectly through changes in human activity at the vicinity of our study sites associated with these
83 climatic changes.

84 Historical Pb contamination associated with mining activities in Poland has been
85 documented. The Rudawy Janowickie Mountains of Silesia, in Southwestern Poland were heavily
86 mined for coal, copper (Cu), iron (Fe), silver (Ag), and zinc-lead (Zn-Pb) ores (e.g. Cabala et al.,
87 2013; Kierczak et al., 2013; Rybicka, 1996). There is historical documentation of ore mining since

88 the 12th century, but there may have been mining activity as early as the 5th century A.D.
89 (Ciarkowska et al., 2016; Kierczak et al., 2013; Kylander et al., 2005; Tyszka et al., 2012). Mining
90 activities were recorded as Pb isotopic ratios and other trace element concentrations in Baltic Sea
91 sediment from the 12th to 17th century A.D. (Zaborska, 2014), and in a bog located in Northern
92 Poland (De Vleeschouwer et al, 2009a, b) from the 9th to 18th century A.D.

93 Previous studies throughout Europe measured Pb isotopes in lake and bog sediment to
94 estimate the importance and origin of anthropogenic Pb (e.g. Martínez Cortizas et al., 2002).
95 Sedimentary records from lake and wetland systems act as environmental archives for local and
96 regional anthropogenic activity over time. Ideal study sites for differentiating between local and
97 regional, anthropogenic and non-anthropogenic Pb sources comprise at least two nearby locations:
98 one rural (relatively pristine) and a second that was influenced by documented human activities.
99 Previous results obtained from sedimentary cores using Pb isotopes from A.D. 500 (post Roman
100 period) to around A.D. 1800 (pre-Industrial Revolution) focus on Western and Central Europe.
101 The few previous studies based to the east of Germany analyzed sediment samples from
102 mountainous regions (Monna et al., 2000; Shotyk, 1998; Véron et al., 2014) and the Baltic Sea
103 (Zillen et al, 2012). Only one study in Northern Poland aimed to track solely regional signals of
104 coal and mining from Southwest Poland (De Vleeschouwer et al., 2009b).

105 No known high temporal resolution data has been previously published for Pb isotopes in
106 the Kulmerland region. The main objective of this research was to quantify anthropogenic Pb
107 pollution over the last 1,500 years at Radzyń Chełmiński, using primarily Pb isotopic signatures.
108 By comparing similar cores from two nearby sites (one in a rural area and a second in the vicinity
109 of a town), we investigated short range (activity from a surrounding town) versus long range
110 (mining signal from Southwestern Poland) transport pollution, as well as potential indirect climatic

111 impacts on human development. Our combination of historical context with detailed geochemical
112 data provide new insights about the extent of local and regional pollution dispersal.

113

114 **2. METHODOLOGY**

115 **2.1 Study Sites**

116 Two distinct ancient lake systems within the Chełmo Land, Kuyavian-Pomeranian
117 Voivodeship, Poland were sampled for this study: Radzyń Chełmiński and Rywałd (Figure 1). **The**
118 **Kuyavian-Pomeranian Voivodeship lies along the border of historic Prussia and Poland. It came**
119 **under Polish control from the mid-10th century and was at the frontier between Polish and Prussian**
120 **territories. There were increasing raids by Prussians into the 12th and early 13th century in**
121 **response to attempts by Poland to conquer Prussian territories, and eventually Konrad I Duke of**
122 **Masovia invited in the Teutonic Order to help defend his territories in the early 1230s – with the**
123 **first timber fortification built at Radzyn in 1234. Historical texts and archaeological studies**
124 **indicate human settlement from the end of the Roman period (around 300 A.D.) to present (e.g.**
125 **Pluskowski, 2013). The wetlands, including the Castle Lake, are now largely infilled and covered**
126 **in sedges, with surface water present to ca. 10–20 cm within the interior of the lake, mostly during**
127 **the wet winter/spring months.**

128 The site at Radzyń Chełmiński lies within 300 m of Radzyń Chełmiński Castle, a Teutonic
129 Order castle built between 1310 and 1340 A.D., and a town of approximately 2,000 inhabitants,
130 settled in concurrence with the settlement of the Teutonic Order (early 13th century; Brown et al.,
131 2015). The castle remained an important commander center into the 15th century, but was

132 dissolved in 1454 during the Thirteen Years War (1454–1466). By the 16th century much of the
133 western wing of the castle was a disused ruin. The castle was partly dismantled in the 19th century.

134 Rywałd, located 7 km due East of Radzyń Chełmiński, is a rural site with evidence of
135 woodland, and minor human impact within the pollen record of the same core during the 11th to
136 12th centuries (Brown et al., 2015). The surrounding area only was used within the past century
137 for agricultural purposes (Brown et al., 2015). The Vistula and Drwęca rivers are in proximity to
138 both sites. The Vistula River runs through the center of the Voivodeship which was once the
139 frontier zone between Slavic Pomerania (East Pomerania), Prussian Pomesania, and Piast Poland
140 (Brown and Pluskowski, 2011; Pluskowski, 2013; Zamoyski, 1987). The underlying sediment is
141 made up of glacial till deposited by the Scandinavian ice sheet during the Vistulian (Weichselian)
142 Glaciation (receded 11,700 years ago; Marks, 2012).

143

144 **2.2 Sampling**

145 Two sediment cores, 100 cm (Radzyń Chełmiński) and 120 cm (Rywałd) depth, were
146 collected in August 2013 from the center of each wetland basin using a Russian auger. The
147 coordinates of the two sequences are 53°22'27.4" N, 19°03'13.7" E (Rywałd) and 53°23' N, 18°56'
148 E (Radzyn). Sampling intervals were adjusted to obtain high-resolution records during the
149 Crusading Period and Teutonic Order occupation focused on the late medieval period (13th to 16th
150 centuries) based on age models derived from radiocarbon dating. For Radzyń Chełmiński and
151 Rywałd, 60 and 59 samples were considered, respectively. In March 2014, “background” samples
152 of glacial sediment at 100-200 cm depth below land surface were collected adjacent to both lakes
153 using a gouge auger to provide the natural background signature for each site. Four background

154 samples for Radzyń were collected at Golebiewko, including 6 subsamples (N 53 degrees 23'39.
155 7" E 018 degrees 59'31. 1"). Three background samples for Rywałd were collected in Rywałd,
156 including 9 subsamples (N 53 degrees 20'58.5" E 019 degrees 05'22.0"). All samples were stored
157 at 4°C prior to analysis.

158

159 2.3 Analyses

160 Sediment cores were logged to determine macroscopic lithofacies. Mastersizer Laser
161 analysis was used to specify particle size within each macro layer. Samples were collected every
162 10 cm for each lithofacies section. Samples were placed on a plastic crucible where a minimal
163 amount of Calgon solution was added and mixed into sample with a rubber stamper until all
164 particles were separated. All organic material and particles above 2mm were removed. The
165 solution was washed with ultra-pure water into the Mastersizer Laser for analysis.

166 Extruded sediment samples dried at room temperature for three days, and homogenized
167 with mortar and pestle prior to digestion. Aliquots of 500 mg for each sample were transferred to
168 digestion tubes and cold digested at room temperature for 12 hours using 10 ml ultra-high purity
169 HNO₃ under clean lab conditions. Tubes were moved to hot baths and heated at 60°C for three
170 hours, then at 110°C for an additional 12 hours. We wanted to extract metal deposition from the
171 sediments bound to organic matter, metal that had adhered to particles as a result of atmospheric
172 deposition and metals and elements bound to sediment surfaces. We did not want to digest all the
173 inorganic, silicate material as this leads to a much more complex Pb isotope signal with the
174 potential to mix from multiple geological sources. Studies have shown (Cook et al. 1997) that hot
175 HNO₃ digestion delivers similar results to other digestion techniques as the bulk of the metal

176 concentration is absorbed to the mineral surfaces and/or in organic matter, not in the mineral
177 silicate components. Digested samples were filtered using a 0.45 µm filter and diluted to 100 ml
178 in ultra-pure water for analysis.

179 Reference materials (Sewage Reference 5RSS53) and full instrument blanks were included
180 for all analyses. In order to quantify the recovery rates from our digestion methods we used an
181 internal sewage sludge standard normalized against an international standard (ERM CC144),
182 which has reported values for extractable metals in sewage sludge. The reason we chose these
183 standards is that they have reported values for both total digestion and extractable metals (using
184 nitric acid), and have relatively high TOC (36 wt %) which was similar to the peaty, organic
185 sediments from the core materials. The reported values for our internal standard (normalized to
186 ERM CC144) for Pb were 118 mg/kg and 8.8 mg/kg for Ti. The average of our extracted values
187 over four runs (n=8) were 128 +/- 13 mg/kg and 9.7 +/- 2.1 mg/kg for Pb and Ti respectively,
188 resulting in a recovery of 108 +/- 9% and 111 +/- 18%, respectively. This indicates that the nitric
189 acid extraction used was capable of liberating all of the available metal components in the organic
190 fraction.

191 Lead and titanium concentrations were determined using a Perkin Optima 7300 Inductively
192 Coupled Plasma – Optical Emission Spectrometer (ICP-OES) at the University of Reading, UK.
193 For each depth horizon, the enrichment factor (E.F.) for Pb was calculated using the equation (1)
194 provided below (Gloaguen and Passe, 2017; N’guessan et al., 2009) and average upper crustal Pb
195 and Ti concentrations (McLennan, 2001). Enrichment Factor quantifies the amount of enrichment
196 of Pb from natural levels within sediment (e.g. Chester and Stoner, 1973, N’guessan et al., 2009):

$$197 \quad EF = \frac{\left(\frac{Pb}{Ti}\right)_{sample}}{\left(\frac{Pb}{Ti}\right)_{upper\ continental\ crust}} \quad (1)$$

198 To determine Pb isotopic compositions, digested samples were further diluted to 4 ppb of
199 Pb for each sample, based on individual Pb concentrations per sample as quantified by ICP-OES,
200 to maintain the same concentration throughout samples. This was done so that Pb concentration
201 would not affect Pb isotope analysis. Reference NIST SRM 981 was used as the external standard
202 for ^{206}Pb , ^{207}Pb , and ^{208}Pb measurements. All analyses were run in bracket configuration (standard-
203 sample-standard) to allow for mass drift correction. Three Pb isotopes, namely ^{206}Pb , ^{207}Pb , and
204 ^{208}Pb , were analyzed via Inductively Coupled Plasma - Mass Spectrometer (ICP-MS)
205 (ThermoFisher iCapQ) equipped with a collision cell. The external calibration standard NIST SRM
206 981 was used to allow for mass drift correction. The mass drift for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ were
207 routinely $<0.5\%$. Two Pb isotope ratios were calculated: $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. These ratios
208 have been the most widely used in similar studies to determine anthropogenic inputs (e.g. Alfonso
209 et al., 2001, Bi et al., 2017, Díaz-Somoano et al., 2009, Monna et al., 2000,).

210

211 **2.4 Sediment Dating**

212 Accelerator Mass Spectrometry (AMS) ^{14}C dating was used to determine absolute age and
213 accumulation rates of sediment. Twelve samples were processed for Radzyń Chełmiński, at 10 cm
214 intervals, with 10 samples taken from Rywałd, at 5-15 cm intervals. Samples for radiocarbon
215 dating were sent to the Scottish Universities Research Centre (SUERC), Glasgow, Scotland. Linear
216 regression modelling was conducted using Bayesian accumulation to provide age-to depth
217 estimations through each core (SI_1; Bacon; Blaauw and Christen, 2011). To represent sediment
218 dates, the notation “A.D.” was used for the age.

219 Reliable chronologies are a fundamental component of palaeoecological investigation of
220 lakes and peat bogs. Terrestrial plant macrofossils are considered the most reliable material for
221 radiocarbon dating (Blaauw et al 2004), although unfortunately none were recovered from either
222 Radzyń or Rywałd. Radiocarbon dates were therefore derived on samples of gyttja (Radzyń) and
223 in the case of Rywałd on both peat and gyttja. Care was taken to identify any potential issues of
224 contamination with old or young. Contamination by young carbon may occur through root
225 penetration, whilst lake sediments may exhibit older radiocarbon ages (reservoir effect) reflecting
226 inclusion of old carbon eroded from calcareous soils/bedrock, or through the uptake of dissolved
227 inorganic carbon by aquatic plants (Björk and Wohlfarth 2004; Butz 2017).

228 Samples of bulk peat from Rywałd are derived from herbaceous fen considered reliable
229 material for radiocarbon dating (e.g. Nilsson et al 2001; Blaauw et al 2004). The peat deposits
230 reflect treeless habitats, although some herbaceous plants growing in fens, such as sedges, have
231 root systems which can penetrate down to 2m, with the potential to introduce young carbon unless
232 removed (e.g. Valiranta et al 2014). However, no roots or evidence for rooting by either trees or
233 herbaceous plants was recorded during the detailed examination and sampling of the cores.

234 The core from Radzyń was the final of three cores (Radzyń 3) sampled and analysed from
235 the Castle lake, with dates derived on gyttja (Radzyń 2 and Radzyń 3) and in the case of the first
236 Radzyń core (Radzyń 1) on both peat and gyttja. Although the occurrence and/or magnitude of a
237 reservoir effect can be difficult to determine without supporting dates from plant macrofossils or
238 lake varves, comparison between the four lake sequences from Radzyń and Rywałd suggest that if
239 present at all, the reservoir effect had a negligible effect on the chronologies. All four sequences
240 show a strong linear progression in radiocarbon dates. There is a high degree of temporal similarity
241 in pollen signals between sites, irrespective of whether dates are derived from peat or gyttja.

242 Similarity is apparent in the timing of key changes in vegetation and land-use, most apparent in
243 the decline in hornbeam, and the onset of major anthropogenic activity from c. AD 1100 (Brown
244 2019); these changes are considered to reflect comparable local-regional processes, reflected with
245 varying magnitude in all four sequences from Radzyń and Rywałd. One could reasonably expect
246 to observe spatial and temporal variations in the magnitude of a reservoir effect, reflecting
247 variation in carbon input within and between sites and pollen sequences as a result of lake
248 catchment, vegetation and land-use (e.g. Tranvik et al 2009; Shou et al 2015) The high degree of
249 similarity therefore argues against a significant reservoir effect at Radzyń and Rywałd.

250

251 **2.5 Modelling**

252 The Bayesian mixing model Food Reconstruction Using Isotopic Transferred Signals
253 (FRUITS; Fernandes et al., 2014) was run with our Pb isotope data ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$)
254 to model the anthropogenic contribution (in % of total Pb) versus time for both sites. Although
255 FRUITS was made for dietary reconstruction, it is a general mixing model suitable for
256 environmental isotopic modeling (e.g. Fernandes et al., 2014). **FRUITS manual recommends to**
257 **not using too many sources vs proxies, no more than +1 (i.e. if you have 2 isotope ratios, you**
258 **shouldn't be asking FRUITS to attribute to more than 3 sources which is our case). For our**
259 **modeling, natural endmembers comprised the mean background values specific to each site. The**
260 **anthropogenic endmember for both sites was calculated from the mean of published Southwest**
261 **Poland coal, ore, and slag lead isotopic signatures (Tyszka et al., 2012). The dust endmember for**
262 **both sites was taken from Veron et al. (2014).**

263

264 3. RESULTS

265 3.1 Sediment Characterization

266 Troel-Smith core logging results show sediment at Radzyń Chełmiński is composed of 1)
267 highly humified *Turfa herbacea* and organic lake mud from 0 to 27 cm with a diffuse boundary;
268 2) organic lake mud with 10% to 1% roots from 27 cm to the bottom of the core. At Rywałd,
269 sediment is composed of 1) *Argilla granosa*: silt with roots to partially humified *Turfa herbacea*
270 peat from 0 to 43 cm with a sharp boundary; 2) silt and clay *argilla* with 5% roots from 43 to 68
271 cm with a sharp boundary; 3) organic lake mud composed of silty sand to sandy silt from 87 cm
272 to the bottom of the core (SI_2, SI_3).

273 According to particle size analyses and the Wentworth scale (Wentworth, 1922), Particle
274 size for both sites ranged from 0.46 to 3080 microns, ranging in grain size class from fine clay to
275 very fine gravel. The average grain size at Radzyń Chełmiński was silt (55.56 to 62 microns) from
276 0 to about 30 cm, and very fine sand (62 microns to 104 microns) from 30 cm to the bottom of the
277 core. Percentages for clay, silt, and sand ranged from 0.67 to 3%, 50 to 69%, and 27 to 49%,
278 respectively. At Rywałd all sediment was very fine sand (62 to 125 microns) apart from 42 cm
279 with an average particle size 126.25 microns (fine sand) (SI_4). Percentages for clay, silt, and sand
280 ranged from 0.02 to 2%, 40 to 61%, and 23 to 50%, respectively.

281

282 3.2 Lead Enrichment Factor and Isotopic Compositions

283 Radzyń Chełmiński and Rywałd profiles for Pb enrichment factor relative to average
284 continental crust (E.F.; McLennan, 2001), and $^{206}\text{Pb}/^{207}\text{Pb}$ are provided in Figure 2. Age values
285 are based on the average age modelled by 2σ Bayesian modelled uncertainties. Lead is enriched

286 by a factor of 14 to 60, and 13 to 159 for Radzyń Chełmiński and Rywałd, respectively. At Rywałd,
287 there is a sharp decrease from ~150 at the top of the core to 75 around A.D. 1980, then further
288 decrease to a minimum Pb E.F. of 37 around A.D. 1755±147. Lead enrichment factor at Rywałd
289 then varies between 33 and 70 down to A.D. 1104±80, increases to the maximum E.F. of 159
290 around A.D. 1024±94, and steadily decreases to 14 (A.D. 731±109), where the Pb E.F. becomes
291 relatively stable around 15±2 to the bottom of the core (A.D. 572±8). At Radzyń Chełmiński, Pb
292 E.F. decreases from 81 at the top of the sediment core to 38 at A.D. 1621 ±166, with a minor
293 increase to 58 (A.D. 1587±148) and continuing decrease to 30 at A.D. 1500±130. Enrichment
294 factor remains relatively stable with minor variations between 11 and 38 down to A.D. 979±102,
295 before decreasing to the minimum value of 14 at A.D. 894±85, maintaining the same Pb E.F. until
296 the bottom of the core (A.D. 803±99).

297 For both sites, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ranges from 1.17 to 1.27‰. At Radzyń Chełmiński,
298 three zones can be defined. From the top of the core the ratio increases with age from 1.18 ‰ to
299 1.27‰ at A.D. 1227±112, then decreases to 1.18‰ at A.D. 934±97. From this minimum, the
300 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio increases to 1.25‰ at the bottom of the core (A.D. 803±99). Five $^{206}\text{Pb}/^{207}\text{Pb}$
301 zones can be identified for Rywałd. From the top of the core to A.D. 1443±114, the isotopic ratio
302 increases from 1.17‰ to 1.21‰, then remains constant at 1.21±0.05‰ down to A.D. 1395±68.
303 The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio continues to increase to 1.25‰ at A.D. 1253±44, decreases to 1.18‰ at A.D.
304 1083±82, remains constant at 1.18‰ to A.D. 768±106, and significantly increases to 1.25‰ at
305 A.D. 572±81. These isotopic profiles are very different from those of previous published data of
306 nearby sites from Northern Poland and Belgium (Fig. 2C; De Vleeschouwer et al., 2009b, Fagel
307 et al., 2014), which show a similar trend to one another over time, with much lower and rather
308 constant $^{206}\text{Pb}/^{207}\text{Pb}$ values (1.14 – 1.18‰) than our new dataset.

309 From the top of both cores to about A.D. 1700, as Pb E.F. decreases, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio
310 increases. Lead E.F. and isotope ratios have a weak negative correlation, with higher Pb E.F.s
311 coinciding with lower $^{206}\text{Pb}/^{207}\text{Pb}$ values.

312

313 4. DISCUSSION

314 4.1 Identification of Lead Sources

315 Three-point plots are a useful approach to differentiating among natural and anthropogenic
316 Pb sources by comparing $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Fig. 3; Alfonso et al., 2001, Bi et al.,
317 2017, Díaz-Somoano et al., 2009, Harlavan et al., 2010, Monna et al., 2000, Zohar et al., 2014).
318 Background sample averages from both sites (natural Pb isotopic ratio endmember: Radzyń
319 Chełmiński: $^{206}\text{Pb}/^{207}\text{Pb} = 1.33 \pm 0.01\text{‰}$; $^{208}\text{Pb}/^{206}\text{Pb} = 1.97 \pm 0.004\text{‰}$; Rywałd: $^{206}\text{Pb}/^{207}\text{Pb} =$
320 $1.30 \pm 0.02\text{‰}$; $^{208}\text{Pb}/^{206}\text{Pb} = 1.96 \pm 0.03\text{‰}$) and Southwest Poland coal, ore, and slag combined
321 average (anthropogenic endmember: $^{206}\text{Pb}/^{207}\text{Pb} = 1.17 \pm 0.01\text{‰}$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.09 \pm 0.01\text{‰}$;
322 Tyszka et al., 2012) were also included in Figure 3. Lead isotopic ratios for both Radzyń
323 Chełmiński fall along a single trend line between the anthropogenic endmember and an
324 endmember similar to the background averages. Due to the glacial till composition of background
325 sediment, Pb isotopic ratios for samples are not perfectly linear with background ratios. Overall,
326 the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ranges from 1.18 to 1.28‰ for Radzyń Chełmiński, and 1.17 to 1.25‰ for
327 Rywałd. The $^{208}\text{Pb}/^{206}\text{Pb}$ ratio for Radzyń Chełmiński ranges from 1.96 to 2.08‰, and 1.98 to
328 2.10‰ for Rywałd. Error bars representing 1 standard deviation for all averages are included
329 (Southern Poland coal, ore and slag $^{206}\text{Pb}/^{207}\text{Pb} = 1.17 \pm 0.01$; $^{208}\text{Pb}/^{206}\text{Pb} = 2.09 \pm 0.01$; Radzyń

330 Chelmiński background $^{206}\text{Pb}/^{207}\text{Pb}=1.33\pm 0.01$; $^{208}\text{Pb}/^{206}\text{Pb}=1.97\pm 0.004$; Rywałd background
331 $^{206}\text{Pb}/^{207}\text{Pb}=1.30\pm 0.03$; $^{208}\text{Pb}/^{206}\text{Pb}=1.96\pm 0.03$).

332 Compared to other similarly aged Central European sedimentary records, our new dataset
333 displays significant differences (e.g. Fagel et al., 2014, Zillen et al., 2012, De Vleeschouwer et al.,
334 2009b). Previously published data from the North Poland Bog (Słowińskie Błoto Bog; De
335 Vleeschouwer et al., 2009b) fall along the same trend line. However, the North Poland bog displays
336 an isotopic composition almost entirely from Southwest Poland coal and ore, indicating a much
337 stronger regional anthropogenic signal, with little to no natural Pb input as indicated in the previous
338 study (Fig. 3; De Vleeschouwer et al., 2009b). In addition, the North Poland Bog indicates an
339 entirely anthropogenic source, with lower $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ than that of the Southwest
340 Poland anthropogenic end members. Such source dissimilarity is expected. Unlike Radzyń
341 Chelmiński and Rywałd, Słowińskie Błoto is a raised (ombrotrophic) peat bog. Signals from peat
342 sediment are expected to record mostly atmospheric inputs (solely rain), versus lake sediment from
343 the current study which include both terrestrial sediment (from runoff) and atmospheric inputs
344 (e.g. Fagel et al., 2014, Thevenon et al., 2011).

345

346 **4.2 Changes in Lead Sources Over Time**

347 **4.2.1 Anthropogenic Sources**

348 Lead isotopic data processed using FRUITS, a Bayesian mixing model, quantified the
349 importance of anthropogenic Pb inputs for each depth sampled (Fig. 4). Climatic periods included
350 in bars below both graphs present cold periods as blue bars, and warm periods as red bars. Arrows
351 along the top of Figure 4 indicate the building of a Teutonic Order fort (A.D. 1234; Urban, 1980)

352 and castle (late 13th century; Urban, 1980) at Radzyń Chełmiński; this activity would not have
353 impacted Rywałd.

354 Modeled anthropogenic Pb contribution is described from oldest to most recent inputs (Fig.
355 4). At Radzyń Chełmiński, the fraction of total lead attributed to anthropogenic inputs in the oldest
356 sediments appears to be influenced by anthropogenic Pb pollution from A.D. 883±99 to A.D.
357 1054±104. Contribution of Southwest Poland coal, ore, and slag during that period reaches a
358 maximum of 35% at A.D. 979±97. The anthropogenic fraction of total Pb remains below 1% from
359 A.D. 1168±114 to with A.D. 1296±94, then increases from the beginning of the 14th century
360 towards a dominantly anthropogenic contribution at the top of the core (up to 65%).

361 At Rywałd, the modeled anthropogenic contribution increases from the core bottom to
362 reach a maximum in A.D. 973±80 of 65%, and decrease to 1% at A.D. 1223±45. Subsequently,
363 the contribution sharply increases to 49% in A.D. 1303±54 and remains relatively stable with an
364 average value of 38±8% to the top of the core, with the exceptions of the two most recent samples
365 (74 and 86%).

366

367 4.2.2 Mining Activity – Long Range Transport

368 Atmospheric anthropogenic Pb signatures are expected to have been transported from
369 regional mines. Approximately 400 km to the south of Radzyń Chełmiński and Rywałd, in the
370 Rudawy Janowickie Mountains of Southwest Poland, a series of mines were active periodically
371 over the last millennium (e.g. Kierczak and Pietranik, 2011). Primary ores from Southwest Poland
372 include bituminous and brown coal, Cu, Zn, and Pb ores, native S, and rock salt (Rybicka, 1996).
373 Samples from Janowice, Wielkie, Szklary, Legnica, Miedzianka, and Wałbrzych sites in

374 Southwest Poland were used to represent an anthropogenic contribution (Fig. 4; Tyszka et al.,
375 2012). These mines are the nearest likely source of anthropogenic Pb in sediments from both
376 Radzyń Chełmiński and Rywałd. Documentation and precise dates are scarce prior to the 1800s,
377 but evidence can be pieced together through the few historical records available and archaeological
378 evidence.

379 First known Zn-Pb ore exploitation in Southwest Poland began in the Cracow-Silesia
380 district during the 12th to 13th centuries (Cabala et al., 2013). Mining and smelting of Cu in the
381 Rudawy Janowickie Mountains has occurred from the 14th century to present (e.g. Bukowski,
382 2011, Kierczak et al., 2013). Miedzianka, in particular was the largest center of mining and
383 smelting Cu, As, and Ag in Silesia, beginning as early as A.D. 1310 (Kierczak and Pietranik,
384 2011). These mining activities are probably responsible for the change in Pb isotopic ratios
385 observed at Rywałd just after A.D. 1200 (Fig. 4). Copper slags were deposited in the mountains
386 from the 14th to 16th century (Kierczak et al., 2013). Exploitation peaked in the 16th century, when
387 resources were exhausted, declining until the end of the 17th century (Kierczak and Pietranik,
388 2011). Our data indicates that this historical record of mining activity resulted in lead pollution
389 throughout the region, as shown by the relatively stable anthropogenic contribution in Rywałd for
390 the same time period followed by a small decrease. Ore mining activities became prevalent again
391 from the beginning of the 18th century to the beginning of the 19th century, focusing on Cu-rich
392 ore, as anthropogenic Pb again increases at Rywałd. Mining and smelting in the Rudawy
393 Janowickie mountains ceased entirely in A.D. 1925 (Kierczak and Pietranik, 2011, Kierczak et al.,
394 2013).

395 Coal exploitation was also prevalent in the Rudawy Janowickie Mountains of Southwest
396 Poland from the 12th century onwards, including two key basins, the Upper Silesian Coal Basin

397 (Bukowski, 2011, Rybicka, 1996) and the Lower Silesian Coal Basin (LSCB; Rybicka, 1996). Ore
398 was also mined in these basins. In Bytom and Olkusz, sub districts of the Upper Silesian Coal
399 Basin, Pb, Zn, and Cd ores were mined since the 12th-14th century (depending on source;
400 Ciarkowska et al., 2016, Rybicka, 1996,).

401 Additionally, from the 1800s onwards, anthropogenic contributions from modern mining,
402 bituminous coal combustion, and leaded gasoline exerted substantial control of the sedimentary
403 Pb isotopic compositions and concentrations at both sites, as documented in previous studies (e.g.
404 De Vleeschouwer et al., 2009b, Fialkiewicz-Koziel et al., 2018).

405 To test our hypothesis, a simple mass-balance calculation was applied. At Radzyn by
406 considering only the first 60 cm with a bulk density of approximately 1000 kg/m³, where a mean
407 increase in total Pb of about 5-10 ppm above baseline values can be observed, and by simplifying
408 the time required to accumulate these sediments to 1000 years, we can estimate an average
409 deposition rate of 3-6 mg.m⁻².y⁻¹. Considering this range of deposition rate, we cannot exclude
410 influences from other sources either local or distant.

411

412 **4.2.3 Land Use within Castle Lake Watershed – Short Range Transport**

413 Earliest palynological records at Radzyń Chełmiński suggest the region was dominated by
414 woodland with evidence of local small-scale agricultural activities present around A.D. 0-700
415 (Brown et al., 2015). The Wielbark culture was present in the area from the 2nd to the 5th century
416 A.D., during the Migration period (A.D. 300 to 700). The 5th to 9th century is marked by
417 archaeological evidence of tumuli and stone graves in the forest surrounding Radzyń Chełmiński,
418 with remains of a Slavonic settlement adjacent to the forest (Samojlik et al., 2013). There is also

419 archaeological evidence of depopulation from the 4th century until Slavic settlement from the 7th
420 century (Buko, 2008). A Slavic stronghold was constructed in proximity to Castle Lake around the
421 late 9th century (e.g. Urban, 1980).

422 Prior to Teutonic settlement, the land surrounding Castle Lake at Radzyń Chełmiński was
423 controlled by a Slavic Stronghold, occupied from the late 9th to mid 12th century when it may have
424 been burnt down in an attack (Brown et al., 2015, Chudziak, 1994). Concurrently, there was an
425 intensification in agricultural activity and decrease in woodland, causing increased soil erosion
426 into the surrounding wetland, as presented by palynological evidence (Brown et al., 2015;
427 Chudziak, 1996). Such erosion and increased land-use may have contributed to a decrease in
428 recorded anthropogenic contribution and Pb concentration at Radzyń Chełmiński. Palynological
429 evidence describes an increasingly open landscape in the pre-Crusading period (11th to 12th
430 century) of both intensifying arable and pastoral activity, with woodland retained on nearby land
431 (Brown et al., 2015).

432 Teutonic influence is documented at the location from A.D. 1234 to around A.D. 1454
433 when the Order ceded the territory to Polish control (Pluskowski, 2013; Urban, 1980). The
434 Crusading period began in A.D. 1230, concurrent with the founding of the Teutonic Order castle
435 and town at Radzyń Chełmiński (Brown et al., 2015). During this period agricultural and pastoral
436 land-use was relatively stable surrounding the Castle Lake (Brown et al., 2015). A timber fort was
437 constructed in A.D. 1234, and the castle was later built between A.D. 1310 and 1340 (e.g. Brown
438 et al., 2015). Previously published palynological evidence from Radzyń Chełmiński recorded
439 changes in vegetation and land use during this period, including a decrease in arboreal pollen and
440 increase in cereal pollen (Brown and Pluskowski, 2011; Pluskowski, 2013). The period between
441 A.D. 1350 and 1400 is known as the “Golden Age” of Teutonic Order influence (e.g. Pluskowski,

442 2013). Heathland developed along with agricultural intensification from the late 14th to 15th
443 century, accompanied by a decrease in woodland area (Brown and Pluskowski, 2011). In addition
444 to landscape changes with the arrival of the Teutonic Order, trade routes also developed by efforts
445 to exploit Prussian resources, adding to human impact from the nearby settlements (Harte and
446 Ponting, 1983). As the frontier land between Teutonic Order Prussia and Poland, the Chełmo land
447 (Kulmerland in German), including Radzyń Chełmiński and Rywałd experienced intermittent
448 raids from Prussian tribes, including the Great Prussian Uprising of the 1260s, and subsequent
449 transformation of the landscape (Lukowski and Zawadzki, 2001; Pluskowski, 2013). Such
450 agricultural intensification and castle building may have contributed to altered the regional
451 anthropogenic isotopic signal from the opening of mines within the sediment records, minimizing
452 the expected increase in anthropogenic Pb contribution that was detected at Rywałd, while at the
453 same time causing an increase in Pb concentration.

454 In A.D. 1410, Radzyń Chełmiński Castle was damaged by Polish-Lithuanians (e.g.
455 Pluskowski, 2013). From A.D. 1412 to 1439, the surrounding landscape was subjected to multiple
456 seasons of crop failure, causing many villages in the area to be covered by woodland by A.D. 1444.
457 The Thirteen Years war occurred shortly after, from A.D. 1453 to 1466, with many conflicts
458 occurring near Radzyń, after which the castle became occupied by Poland (e.g. Pluskowski, 2013),
459 falling into ruin by the 16th century (Brown et al., 2015). Further damage occurred during the
460 Swedish Invasion from A.D. 1626 to 1629 (e.g. Brown et al., 2015). Wooded areas contribute
461 minimal weathered and eroded sediment to the surrounding basin, compared to predominantly
462 open fields (arable and pastoral land). The decrease in local influence from the nearby castle and
463 town, and re-establishment of woodlands, may have allowed for a return to a predominantly
464 regional, atmospheric Pb-derived signal in the sediment record during this period.

465

466 **4.2.4 Regional Climatic Influence**

467 Differentiating between climatic and historical influences remains challenging. Although
468 Pb isotopes are not climate proxies, it is possible climate change **or influencing meteorological**
469 **conditions (e.g. change in dominant wind direction patterns, increase in rainfall, flood events, etc.)**
470 might indirectly influence Pb isotopic signatures by promoting the development of human
471 activities (e.g. Büntgen et al., 2016, 2011), mostly during warmer and dryer periods. According to
472 our sediment data (SI_2, SI_3), the Radzyń Chełmiński core is made entirely of lake
473 mud/sediment; while Rywałd contains peat sediment from 0 to 68 cm, and lake mud/sediment
474 from 68 cm to the bottom of the core.

475 Sedimentary records for both cores span five climatic periods: 1) Late Antique Little Ice
476 Age (LALIA, A.D. 536 to 660; e.g. Berglund et al., 2003; Büntgen et al., 2016); 2) the Climatic
477 Optimum in Prussia (COP, A.D. 800 to 1150; e.g. Pluskowski, 2013); 3) the Medieval Warm
478 Period (MWP; A.D. 800 to 1300; e.g. De Vleeschouwer et al., 2009b); 4) the Little Ice Age (LIA;
479 A.D. 1300 to 1850; e.g. De Vleeschouwer et al., 2009b; Hegerl et al., 2017; Lockwood, 2001);
480 and 5) Global Warming (GW; A.D. 1890 to present; e.g. Chiriloaei et al., 2012; Hegerl et al.,
481 2017). Unlike in Western Europe, Prussian communities did not experience a regression after the
482 medieval warm period, and instead thrived (Pluskowski, 2013). We hypothesize that promotion of
483 human activities during favorable climatic conditions (Büntgen et al., 2016) included behaviors
484 that mobilize lead, such as coal burning and ore utilization.

485

486 **5. CONCLUSION**

487 In this study, Pb concentrations and isotope ratios were used to quantify anthropogenic lead
488 inputs and sources, as well as to identify trends in human activity in Northern Poland over the last
489 1,500 years. The use of a rural lake sediment core at Rywałd and a lake core influenced by a nearby
490 town and Teutonic Order castle at Radzyń Chełmiński enabled differentiation between local and
491 regional anthropogenic inputs.

492 Two primary Pb sources have been identified: (1) coal, ore, and slag originated from
493 Southwestern Poland mining activities (long range transport); and (2) erosion from the surrounding
494 watershed associated with the development of human activities (short range transport). High
495 anthropogenic Pb contributions from the 9th to 11th centuries A.D., in the absence of historical
496 evidence for mining activity in Southwestern Poland, point to a previously-unrecognized,
497 substantial anthropogenic pb source during that time period. Local activities dominated the Pb
498 isotopic record from the 11th to 13th centuries A.D., during periods of Slavic and subsequent
499 Teutonic Order settlement and castle building, and agricultural intensification. The long range,
500 anthropogenic, mining signal was elevated around the 16th and 18th to 19th centuries A.D., during
501 periods of decreased local human agricultural activity.

502 Overall, the sediments at Rywałd recorded mostly long range mining inputs originating
503 from Southwest Poland, while Radzyń Chełmiński sediments recorded both sources long range
504 mining signal and local signal from an increase in agricultural and other human activities related
505 to the development of the town and castle. Further studies are required to identify the sources
506 responsible for the anthropogenic signal observed for our sites prior to A.D. 1000.

507

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515

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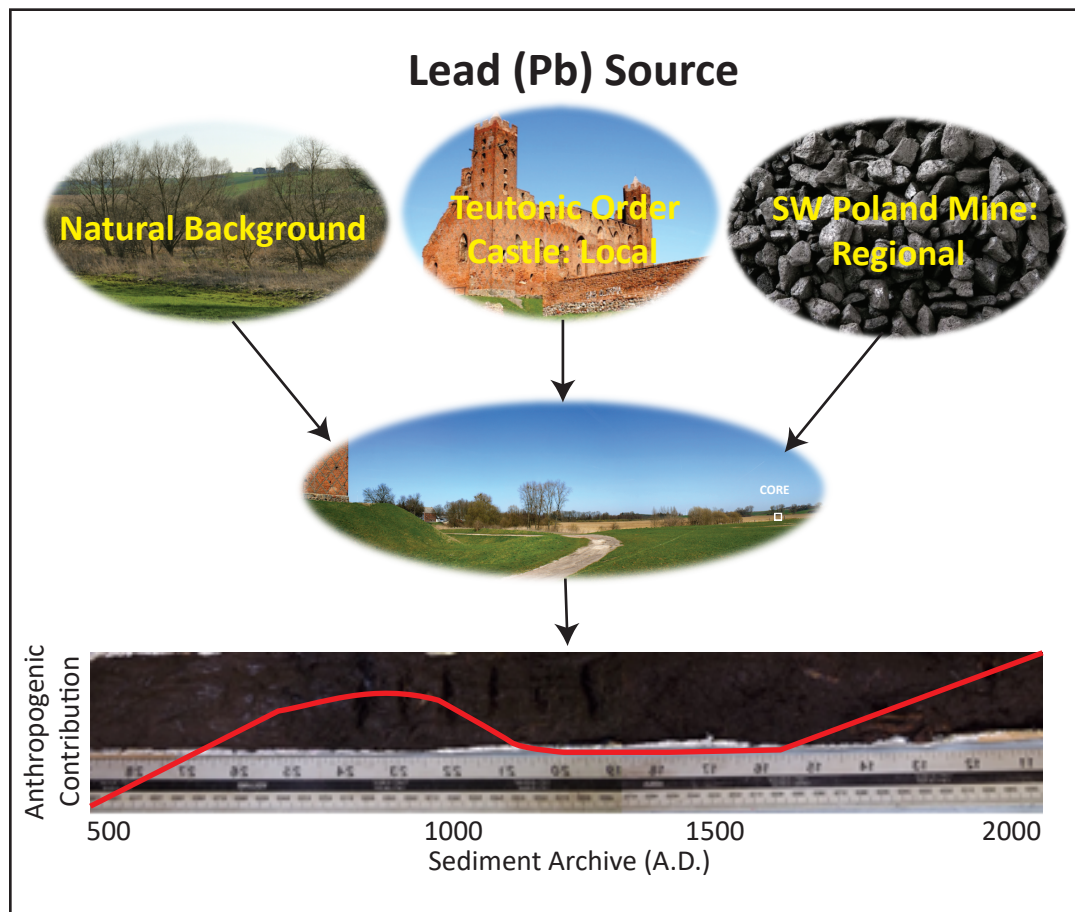
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Highlights

- 1,500 years of paleo-reconstruction using lead isotopes
- Mining contributed significantly to the lead inventory as early as the 13th century via long range transport
- Warmer climate in between 800 and 1,000 A.D. may have favored anthropogenic activities

21 For both sites, Pb enrichment factors relative to titanium (Ti) and upper continental crust
22 values range from 13 to 159. Lead isotopic ratios range from background, pre-anthropogenic local
23 values ($^{206}\text{Pb}/^{207}\text{Pb} = 1.31 \pm 0.03\%$, $^{208}\text{Pb}/^{206}\text{Pb} = 1.97 \pm 0.04\%$) to anthropogenic values (SW
24 Poland coal, ore, slag $^{206}\text{Pb}/^{207}\text{Pb} = 1.17 \pm 0.01\%$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.09 \pm 0.01\%$). Modeled
25 anthropogenic contribution varies greatly over time, ranging from 14 to 100%. At Radzyń
26 Chełmiński, modeled anthropogenic Pb contribution and measured Pb concentration follow
27 similar trends. However, at Rywałd, from around A.D.1000 to A.D. 1400 these profiles diverge
28 significantly. Our new insights highlight different sources of Pb from the 12th century to present
29 day: (1) short range agricultural activities from the town, and (2) long range mining activities.
30 Additionally, prior to the 12th century, our data suggest continental anthropogenic activity possibly
31 favored by a warmer climate.

32

33 **KEYWORDS**

34 Lead – Isotopes – Sediments – Anthropogenic – Sources – Medieval

35

36 **1. INTRODUCTION**

37 Lead (Pb) is a toxic, non-essential, trace element particularly useful for tracking
38 anthropogenic input in environmental archives (e.g. Lanphear et al., 2005). Using Pb isotopes, we
39 can differentiate between anthropogenic (industrial and mining activities, coal and fuel burning;
40 e.g. Cheng and Hu, 2010) and natural sources (i.e. natural weathering processes) that release Pb
41 into the environment (Grousset et al., 1994; Thevenon et al., 2011; Zohar et al., 2014); and as a

42 result, hypothesize on the timing and locations of past human activities (Fagel et al., 2014; Hosono
43 et al., 2016; Zohar et al., 2014).

44 Three radioisotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) are commonly measured for this type of study
45 (Alfonso et al., 2001; Komarek et al., 2008; Reimann et al., 2012). Due to the durations of their
46 half-lives, these isotopes are considered meta-stable in geologically recent sediment (e.g. Russell
47 and Farquhar, 1960). There are no known environmental or industrial processes that fractionate
48 Pb isotopes, and thus the isotopic composition of Pb is affected by Pb source and geologic location
49 (Cheng and Hu, 2010; Doe, 1970; Flegal and Smith, 1995). Additionally, Pb is relatively stable
50 within the sediment column and not readily susceptible to remobilization by early diagenetic
51 processes or biological activities (Audry et al., 2011; Gallon et al., 2004; Harlavan, 1998; Huerta-
52 Diaz, 1998; McIntyre and Gueguen, 2013; Schultz et al., 1987; Tessier et al., 1996;). By analyzing
53 ratios of these three isotopes: $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, it is possible to assess how source
54 contributions of Pb have changed over time for a given location (Baron et al., 2006; Harlavan et
55 al., 2010; Zohar et al., 2014).

56 Within the environment, Pb isotope ratios may be influenced by local, regional, or global
57 sources (e.g. Choi et al., 2007, Martinez Cortizas et al., 2002, 2016, Mil-Homens et al., 2013,
58 2017). For example, In the Iberian Peninsula a number of studies have used Pb isotope ratios to
59 document evidence of regional metallurgy and mining from the Chalcolithic (~3000 BC) to
60 modern period (last 200 years; Martinez Cortizas et al., 2002, 2016, Mil-Homens et al., 2013). In
61 marine sediment within the Portuguese Margin, Pb isotope ratios were also able to record Roman
62 and modern mining activities from the adjacent Iberian region (Mil-Homens et al., 2017, (Include
63 examples from above refs.) Global signatures from atmospheric transport and deposition of Pb,
64 such as Saharan dust storms, and leaded gasoline emissions in modern times, has also been

65 documented (e.g. Bi et al., 2017, Mil-Homens et al., 2017, Shotyk et al., 1998). For this study,
66 regional sources are defined as mining of coal ore, smelting, and leaded gasoline exhaust.
67 Historical mining activities 300 to 500 km to the southwest of the study site may have introduced
68 Pb to the atmosphere, allowing for transport downwind to the study site. This Pb transported over
69 long range is deposited, via association with sinking particles, in lake and peat sediments (e.g.
70 Novak et al., 2003). Local sources, on the scale of kilometers or less, can also contribute to Pb
71 enrichments and/or changes in the Pb isotope ratios in sediments. They include enhanced
72 weathering and erosion of the surrounding landscape due to agricultural activities, building
73 development, metalwork, and domestic coal burning.

74 Regional patterns of Pb transport are of particular interest in Poland due to Poland's unique
75 climatic signal in comparison to the rest of Europe, which is sensitive to both oceanic and
76 continental influences (e.g. Zamoyski, 1987). Specifically, the Medieval Warm Period (MWP)
77 ended in Poland earlier than the rest of Europe (Medieval Warm Period: MWP; A.D. 800 to 1300;
78 e.g. De Vleeschouwer et al., 2009a). The portion of the MWP that influenced Poland is known as
79 the Climatic Optimum in Poland (COP, A.D. 800 to 1150; e.g. Pluskowski, 2013). These climatic
80 patterns may have played two non-mutually exclusive impacts on anthropogenic Pb contributions:
81 directly by impacting efficiency of atmospheric Pb long range transport from mining regions, and
82 indirectly through changes in human activity at the vicinity of our study sites associated with these
83 climatic changes.

84 Historical Pb contamination associated with mining activities in Poland has been
85 documented. The Rudawy Janowickie Mountains of Silesia, in Southwestern Poland were heavily
86 mined for coal, copper (Cu), iron (Fe), silver (Ag), and zinc-lead (Zn-Pb) ores (e.g. Cabala et al.,
87 2013; Kierczak et al., 2013; Rybicka, 1996). There is historical documentation of ore mining since

88 the 12th century, but there may have been mining activity as early as the 5th century A.D.
89 (Ciarkowska et al., 2016; Kierczak et al., 2013; Kylander et al., 2005; Tyszka et al., 2012). Mining
90 activities were recorded as Pb isotopic ratios and other trace element concentrations in Baltic Sea
91 sediment from the 12th to 17th century A.D. (Zaborska, 2014), and in a bog located in Northern
92 Poland (De Vleeschouwer et al, 2009a, b) from the 9th to 18th century A.D.

93 Previous studies throughout Europe measured Pb isotopes in lake and bog sediment to
94 estimate the importance and origin of anthropogenic Pb (e.g. Martínez Cortizas et al., 2002).
95 Sedimentary records from lake and wetland systems act as environmental archives for local and
96 regional anthropogenic activity over time. Ideal study sites for differentiating between local and
97 regional, anthropogenic and non-anthropogenic Pb sources comprise at least two nearby locations:
98 one rural (relatively pristine) and a second that was influenced by documented human activities.
99 Previous results obtained from sedimentary cores using Pb isotopes from A.D. 500 (post Roman
100 period) to around A.D. 1800 (pre-Industrial Revolution) focus on Western and Central Europe.
101 The few previous studies based to the east of Germany analyzed sediment samples from
102 mountainous regions (Monna et al., 2000; Shotyk, 1998; Véron et al., 2014) and the Baltic Sea
103 (Zillen et al, 2012). Only one study in Northern Poland aimed to track solely regional signals of
104 coal and mining from Southwest Poland (De Vleeschouwer et al., 2009b).

105 No known high temporal resolution data has been previously published for Pb isotopes in
106 the Kulmerland region. The main objective of this research was to quantify anthropogenic Pb
107 pollution over the last 1,500 years at Radzyń Chełmiński, using primarily Pb isotopic signatures.
108 By comparing similar cores from two nearby sites (one in a rural area and a second in the vicinity
109 of a town), we investigated short range (activity from a surrounding town) versus long range
110 (mining signal from Southwestern Poland) transport pollution, as well as potential indirect climatic

111 impacts on human development. Our combination of historical context with detailed geochemical
112 data provide new insights about the extent of local and regional pollution dispersal.

113

114 **2. METHODOLOGY**

115 **2.1 Study Sites**

116 Two distinct ancient lake systems within the Chełmo Land, Kuyavian-Pomeranian
117 Voivodeship, Poland were sampled for this study: Radzyń Chełmiński and Rywałd (Figure 1). The
118 Kuyavian-Pomeranian Voivodeship lies along the border of historic Prussia and Poland. It came
119 under Polish control from the mid-10th century and was at the frontier between Polish and Prussian
120 territories. There were increasing raids by Prussians into the 12th and early 13th century in
121 response to attempts by Poland to conquer Prussian territories, and eventually Konrad I Duke of
122 Masovia invited in the Teutonic Order to help defend his territories in the early 1230s – with the
123 first timber fortification built at Radzyn in 1234. Historical texts and archaeological studies
124 indicate human settlement from the end of the Roman period (around 300 A.D.) to present (e.g.
125 Pluskowski, 2013). The wetlands, including the Castle Lake, are now largely infilled and covered
126 in sedges, with surface water present to ca. 10–20 cm within the interior of the lake, mostly during
127 the wet winter/spring months.

128 The site at Radzyń Chełmiński lies within 300 m of Radzyń Chełmiński Castle, a Teutonic
129 Order castle built between 1310 and 1340 A.D., and a town of approximately 2,000 inhabitants,
130 settled in concurrence with the settlement of the Teutonic Order (early 13th century; Brown et al.,
131 2015). The castle remained an important commander center into the 15th century, but was

132 dissolved in 1454 during the Thirteen Years War (1454–1466). By the 16th century much of the
133 western wing of the castle was a disused ruin. The castle was partly dismantled in the 19th century.

134 Rywałd, located 7 km due East of Radzyń Chełmiński, is a rural site with evidence of
135 woodland, and minor human impact within the pollen record of the same core during the 11th to
136 12th centuries (Brown et al., 2015). The surrounding area only was used within the past century
137 for agricultural purposes (Brown et al., 2015). The Vistula and Drwęca rivers are in proximity to
138 both sites. The Vistula River runs through the center of the Voivodeship which was once the
139 frontier zone between Slavic Pomerania (East Pomerania), Prussian Pomesania, and Piast Poland
140 (Brown and Pluskowski, 2011; Pluskowski, 2013; Zamoyski, 1987). The underlying sediment is
141 made up of glacial till deposited by the Scandinavian ice sheet during the Vistulian (Weichselian)
142 Glaciation (receded 11,700 years ago; Marks, 2012).

143

144 **2.2 Sampling**

145 Two sediment cores, 100 cm (Radzyń Chełmiński) and 120 cm (Rywałd) depth, were
146 collected in August 2013 from the center of each wetland basin using a Russian auger. The
147 coordinates of the two sequences are 53°22'27.4" N, 19°03'13.7" E (Rywałd) and 53°23' N, 18°56'
148 E (Radzyn). Sampling intervals were adjusted to obtain high-resolution records during the
149 Crusading Period and Teutonic Order occupation focused on the late medieval period (13th to 16th
150 centuries) based on age models derived from radiocarbon dating. For Radzyń Chełmiński and
151 Rywałd, 60 and 59 samples were considered, respectively. In March 2014, “background” samples
152 of glacial sediment at 100-200 cm depth below land surface were collected adjacent to both lakes
153 using a gouge auger to provide the natural background signature for each site. Four background

154 samples for Radzyń were collected at Golebiewko, including 6 subsamples (N 53 degrees 23'39.
155 7" E 018 degrees 59'31. 1"). Three background samples for Rywałd were collected in Rywałd,
156 including 9 subsamples (N 53 degrees 20'58.5" E 019 degrees 05'22.0"). All samples were stored
157 at 4°C prior to analysis.

158

159 **2.3 Analyses**

160 Sediment cores were logged to determine macroscopic lithofacies. Mastersizer Laser
161 analysis was used to specify particle size within each macro layer. Samples were collected every
162 10 cm for each lithofacies section. Samples were placed on a plastic crucible where a minimal
163 amount of Calgon solution was added and mixed into sample with a rubber stamper until all
164 particles were separated. All organic material and particles above 2mm were removed. The
165 solution was washed with ultra-pure water into the Mastersizer Laser for analysis.

166 Extruded sediment samples dried at room temperature for three days, and homogenized
167 with mortar and pestle prior to digestion. Aliquots of 500 mg for each sample were transferred to
168 digestion tubes and cold digested at room temperature for 12 hours using 10 ml ultra-high purity
169 HNO₃ under clean lab conditions. Tubes were moved to hot baths and heated at 60°C for three
170 hours, then at 110°C for an additional 12 hours. We wanted to extract metal deposition from the
171 sediments bound to organic matter, metal that had adhered to particles as a result of atmospheric
172 deposition and metals and elements bound to sediment surfaces. We did not want to digest all the
173 inorganic, silicate material as this leads to a much more complex Pb isotope signal with the
174 potential to mix from multiple geological sources. Studies have shown (Cook et al. 1997) that hot
175 HNO₃ digestion delivers similar results to other digestion techniques as the bulk of the metal

176 concentration is absorbed to the mineral surfaces and/or in organic matter, not in the mineral
177 silicate components. Digested samples were filtered using a 0.45 µm filter and diluted to 100 ml
178 in ultra-pure water for analysis.

179 Reference materials (Sewage Reference 5RSS53) and full instrument blanks were included
180 for all analyses. In order to quantify the recovery rates from our digestion methods we used an
181 internal sewage sludge standard normalized against an international standard (ERM CC144),
182 which has reported values for extractable metals in sewage sludge. The reason we chose these
183 standards is that they have reported values for both total digestion and extractable metals (using
184 nitric acid), and have relatively high TOC (36 wt %) which was similar to the peaty, organic
185 sediments from the core materials. The reported values for our internal standard (normalized to
186 ERM CC144) for Pb were 118 mg/kg and 8.8 mg/kg for Ti. The average of our extracted values
187 over four runs (n=8) were 128 +/- 13 mg/kg and 9.7 +/- 2.1 mg/kg for Pb and Ti respectively,
188 resulting in a recovery of 108 +/- 9% and 111 +/- 18%, respectively. This indicates that the nitric
189 acid extraction used was capable of liberating all of the available metal components in the organic
190 fraction.

191 Lead and titanium concentrations were determined using a Perkin Optima 7300 Inductively
192 Coupled Plasma – Optical Emission Spectrometer (ICP-OES) at the University of Reading, UK.
193 For each depth horizon, the enrichment factor (E.F.) for Pb was calculated using the equation (1)
194 provided below (Gloaguen and Passe, 2017; N’guessan et al., 2009) and average upper crustal Pb
195 and Ti concentrations (McLennan, 2001). Enrichment Factor quantifies the amount of enrichment
196 of Pb from natural levels within sediment (e.g. Chester and Stoner, 1973, N’guessan et al., 2009):

$$197 \quad EF = \frac{\left(\frac{Pb}{Ti}\right)_{sample}}{\left(\frac{Pb}{Ti}\right)_{upper\ continental\ crust}} \quad (1)$$

198 To determine Pb isotopic compositions, digested samples were further diluted to 4 ppb of
199 Pb for each sample, based on individual Pb concentrations per sample as quantified by ICP-OES,
200 to maintain the same concentration throughout samples. This was done so that Pb concentration
201 would not affect Pb isotope analysis. Reference NIST SRM 981 was used as the external standard
202 for ^{206}Pb , ^{207}Pb , and ^{208}Pb measurements. All analyses were run in bracket configuration (standard-
203 sample-standard) to allow for mass drift correction. Three Pb isotopes, namely ^{206}Pb , ^{207}Pb , and
204 ^{208}Pb , were analyzed via Inductively Coupled Plasma - Mass Spectrometer (ICP-MS)
205 (ThermoFisher iCapQ) equipped with a collision cell. The external calibration standard NIST SRM
206 981 was used to allow for mass drift correction. The mass drift for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ were
207 routinely $<0.5\%$. Two Pb isotope ratios were calculated: $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. These ratios
208 have been the most widely used in similar studies to determine anthropogenic inputs (e.g. Alfonso
209 et al., 2001, Bi et al., 2017, Díaz-Somoano et al., 2009, Monna et al., 2000,).

210

211 **2.4 Sediment Dating**

212 Accelerator Mass Spectrometry (AMS) ^{14}C dating was used to determine absolute age and
213 accumulation rates of sediment. Twelve samples were processed for Radzyń Chełmiński, at 10 cm
214 intervals, with 10 samples taken from Rywałd, at 5-15 cm intervals. Samples for radiocarbon
215 dating were sent to the Scottish Universities Research Centre (SUERC), Glasgow, Scotland. Linear
216 regression modelling was conducted using Bayesian accumulation to provide age-to depth
217 estimations through each core (SI_1; Bacon; Blaauw and Christen, 2011). To represent sediment
218 dates, the notation “A.D.” was used for the age.

219 Reliable chronologies are a fundamental component of palaeoecological investigation of
220 lakes and peat bogs. Terrestrial plant macrofossils are considered the most reliable material for
221 radiocarbon dating (Blaauw et al 2004), although unfortunately none were recovered from either
222 Radzyń or Rywałd. Radiocarbon dates were therefore derived on samples of gyttja (Radzyń) and
223 in the case of Rywałd on both peat and gyttja. Care was taken to identify any potential issues of
224 contamination with old or young. Contamination by young carbon may occur through root
225 penetration, whilst lake sediments may exhibit older radiocarbon ages (reservoir effect) reflecting
226 inclusion of old carbon eroded from calcareous soils/bedrock, or through the uptake of dissolved
227 inorganic carbon by aquatic plants (Björk and Wohlfarth 2004; Butz 2017).

228 Samples of bulk peat from Rywałd are derived from herbaceous fen considered reliable
229 material for radiocarbon dating (e.g. Nilsson et al 2001; Blaauw et al 2004). The peat deposits
230 reflect treeless habitats, although some herbaceous plants growing in fens, such as sedges, have
231 root systems which can penetrate down to 2m, with the potential to introduce young carbon unless
232 removed (e.g. Valiranta et al 2014). However, no roots or evidence for rooting by either trees or
233 herbaceous plants was recorded during the detailed examination and sampling of the cores.

234 The core from Radzyń was the final of three cores (Radzyń 3) sampled and analysed from
235 the Castle lake, with dates derived on gyttja (Radzyń 2 and Radzyń 3) and in the case of the first
236 Radzyń core (Radzyń 1) on both peat and gyttja. Although the occurrence and/or magnitude of a
237 reservoir effect can be difficult to determine without supporting dates from plant macrofossils or
238 lake varves, comparison between the four lake sequences from Radzyń and Rywałd suggest that if
239 present at all, the reservoir effect had a negligible effect on the chronologies. All four sequences
240 show a strong linear progression in radiocarbon dates. There is a high degree of temporal similarity
241 in pollen signals between sites, irrespective of whether dates are derived from peat or gyttja.

242 Similarity is apparent in the timing of key changes in vegetation and land-use, most apparent in
243 the decline in hornbeam, and the onset of major anthropogenic activity from c. AD 1100 (Brown
244 2019); these changes are considered to reflect comparable local-regional processes, reflected with
245 varying magnitude in all four sequences from Radzyń and Rywałd. One could reasonably expect
246 to observe spatial and temporal variations in the magnitude of a reservoir effect, reflecting
247 variation in carbon input within and between sites and pollen sequences as a result of lake
248 catchment, vegetation and land-use (e.g. Tranvik et al 2009; Shou et al 2015) The high degree of
249 similarity therefore argues against a significant reservoir effect at Radzyń and Rywałd.

250

251 **2.5 Modelling**

252 The Bayesian mixing model Food Reconstruction Using Isotopic Transferred Signals
253 (FRUITS; Fernandes et al., 2014) was run with our Pb isotope data ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$)
254 to model the anthropogenic contribution (in % of total Pb) versus time for both sites. Although
255 FRUITS was made for dietary reconstruction, it is a general mixing model suitable for
256 environmental isotopic modeling (e.g. Fernandes et al., 2014). FRUITS manual recommends to
257 not using too many sources vs proxies, no more than +1 (i.e. if you have 2 isotope ratios, you
258 shouldn't be asking FRUITS to attribute to more than 3 sources which is our case). For our
259 modeling, natural endmembers comprised the mean background values specific to each site. The
260 anthropogenic endmember for both sites was calculated from the mean of published Southwest
261 Poland coal, ore, and slag lead isotopic signatures (Tyszka et al., 2012). The dust endmember for
262 both sites was taken from Veron et al. (2014).

263

264 3. RESULTS

265 3.1 Sediment Characterization

266 Troel-Smith core logging results show sediment at Radzyń Chełmiński is composed of 1)
267 highly humified *Turfa herbacea* and organic lake mud from 0 to 27 cm with a diffuse boundary;
268 2) organic lake mud with 10% to 1% roots from 27 cm to the bottom of the core. At Rywałd,
269 sediment is composed of 1) *Argilla granosa*: silt with roots to partially humified *Turfa herbacea*
270 peat from 0 to 43 cm with a sharp boundary; 2) silt and clay *argilla* with 5% roots from 43 to 68
271 cm with a sharp boundary; 3) organic lake mud composed of silty sand to sandy silt from 87 cm
272 to the bottom of the core (SI_2, SI_3).

273 According to particle size analyses and the Wentworth scale (Wentworth, 1922), Particle
274 size for both sites ranged from 0.46 to 3080 microns, ranging in grain size class from fine clay to
275 very fine gravel. The average grainsize at Radzyń Chełmiński was silt (55.56 to 62 microns) from
276 0 to about 30 cm, and very fine sand (62 microns to 104 microns) from 30 cm to the bottom of the
277 core. Percentages for clay, silt, and sand ranged from 0.67 to 3%, 50 to 69%, and 27 to 49%,
278 respectively. At Rywałd all sediment was very fine sand (62 to 125 microns) apart from 42 cm
279 with an average particle size 126.25 microns (fine sand) (SI_4). Percentages for clay, silt, and sand
280 ranged from 0.02 to 2%, 40 to 61%, and 23 to 50%, respectively.

281

282 3.2 Lead Enrichment Factor and Isotopic Compositions

283 Radzyń Chełmiński and Rywałd profiles for Pb enrichment factor relative to average
284 continental crust (E.F.; McLennan, 2001), and $^{206}\text{Pb}/^{207}\text{Pb}$ are provided in Figure 2. Age values
285 are based on the average age modelled by 2σ Bayesian modelled uncertainties. Lead is enriched

286 by a factor of 14 to 60, and 13 to 159 for Radzyń Chełmiński and Rywałd, respectively. At Rywałd,
287 there is a sharp decrease from ~150 at the top of the core to 75 around A.D. 1980, then further
288 decrease to a minimum Pb E.F. of 37 around A.D. 1755±147. Lead enrichment factor at Rywałd
289 then varies between 33 and 70 down to A.D. 1104±80, increases to the maximum E.F. of 159
290 around A.D. 1024±94, and steadily decreases to 14 (A.D. 731±109), where the Pb E.F. becomes
291 relatively stable around 15±2 to the bottom of the core (A.D. 572±8). At Radzyń Chełmiński, Pb
292 E.F. decreases from 81 at the top of the sediment core to 38 at A.D. 1621 ±166, with a minor
293 increase to 58 (A.D. 1587±148) and continuing decrease to 30 at A.D. 1500±130. Enrichment
294 factor remains relatively stable with minor variations between 11 and 38 down to A.D. 979±102,
295 before decreasing to the minimum value of 14 at A.D. 894±85, maintaining the same Pb E.F. until
296 the bottom of the core (A.D. 803±99).

297 For both sites, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ranges from 1.17 to 1.27‰. At Radzyń Chełmiński,
298 three zones can be defined. From the top of the core the ratio increases with age from 1.18 ‰ to
299 1.27‰ at A.D. 1227±112, then decreases to 1.18‰ at A.D. 934±97. From this minimum, the
300 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio increases to 1.25‰ at the bottom of the core (A.D. 803±99). Five $^{206}\text{Pb}/^{207}\text{Pb}$
301 zones can be identified for Rywałd. From the top of the core to A.D. 1443±114, the isotopic ratio
302 increases from 1.17‰ to 1.21‰, then remains constant at 1.21±0.05‰ down to A.D. 1395±68.
303 The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio continues to increase to 1.25‰ at A.D. 1253±44, decreases to 1.18‰ at A.D.
304 1083±82, remains constant at 1.18‰ to A.D. 768±106, and significantly increases to 1.25‰ at
305 A.D. 572±81. These isotopic profiles are very different from those of previous published data of
306 nearby sites from Northern Poland and Belgium (Fig. 2C; De Vleeschouwer et al., 2009b, Fagel
307 et al., 2014), which show a similar trend to one another over time, with much lower and rather
308 constant $^{206}\text{Pb}/^{207}\text{Pb}$ values (1.14 – 1.18‰) than our new dataset.

309 From the top of both cores to about A.D. 1700, as Pb E.F. decreases, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio
310 increases. Lead E.F. and isotope ratios have a weak negative correlation, with higher Pb E.F.s
311 coinciding with lower $^{206}\text{Pb}/^{207}\text{Pb}$ values.

312

313 **4. DISCUSSION**

314 **4.1 Identification of Lead Sources**

315 Three-point plots are a useful approach to differentiating among natural and anthropogenic
316 Pb sources by comparing $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Fig. 3; Alfonso et al., 2001, Bi et al.,
317 2017, Díaz-Somoano et al., 2009, Harlavan et al., 2010, Monna et al., 2000, Zohar et al., 2014).
318 Background sample averages from both sites (natural Pb isotopic ratio endmember: Radzyń
319 Chełmiński: $^{206}\text{Pb}/^{207}\text{Pb} = 1.33 \pm 0.01\text{‰}$; $^{208}\text{Pb}/^{206}\text{Pb} = 1.97 \pm 0.004\text{‰}$; Rywałd: $^{206}\text{Pb}/^{207}\text{Pb} =$
320 $1.30 \pm 0.02\text{‰}$; $^{208}\text{Pb}/^{206}\text{Pb} = 1.96 \pm 0.03\text{‰}$) and Southwest Poland coal, ore, and slag combined
321 average (anthropogenic endmember: $^{206}\text{Pb}/^{207}\text{Pb} = 1.17 \pm 0.01\text{‰}$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.09 \pm 0.01\text{‰}$;
322 Tyszka et al., 2012) were also included in Figure 3. Lead isotopic ratios for both Radzyń
323 Chełmiński fall along a single trend line between the anthropogenic endmember and an
324 endmember similar to the background averages. Due to the glacial till composition of background
325 sediment, Pb isotopic ratios for samples are not perfectly linear with background ratios. Overall,
326 the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ranges from 1.18 to 1.28‰ for Radzyń Chełmiński, and 1.17 to 1.25‰ for
327 Rywałd. The $^{208}\text{Pb}/^{206}\text{Pb}$ ratio for Radzyń Chełmiński ranges from 1.96 to 2.08‰, and 1.98 to
328 2.10‰ for Rywałd. Error bars representing 1 standard deviation for all averages are included
329 (Southern Poland coal, ore and slag $^{206}\text{Pb}/^{207}\text{Pb} = 1.17 \pm 0.01$; $^{208}\text{Pb}/^{206}\text{Pb} = 2.09 \pm 0.01$; Radzyń

330 Chelmiński background $^{206}\text{Pb}/^{207}\text{Pb}=1.33\pm 0.01$; $^{208}\text{Pb}/^{206}\text{Pb}=1.97\pm 0.004$; Rywałd background
331 $^{206}\text{Pb}/^{207}\text{Pb}=1.30\pm 0.03$; $^{208}\text{Pb}/^{206}\text{Pb}=1.96\pm 0.03$).

332 Compared to other similarly aged Central European sedimentary records, our new dataset
333 displays significant differences (e.g. Fagel et al., 2014, Zillen et al., 2012, De Vleeschouwer et al.,
334 2009b). Previously published data from the North Poland Bog (Słowińskie Błoto Bog; De
335 Vleeschouwer et al., 2009b) fall along the same trend line. However, the North Poland bog displays
336 an isotopic composition almost entirely from Southwest Poland coal and ore, indicating a much
337 stronger regional anthropogenic signal, with little to no natural Pb input as indicated in the previous
338 study (Fig. 3; De Vleeschouwer et al., 2009b). In addition, the North Poland Bog indicates an
339 entirely anthropogenic source, with lower $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ than that of the Southwest
340 Poland anthropogenic end members. Such source dissimilarity is expected. Unlike Radzyń
341 Chelmiński and Rywałd, Słowińskie Błoto is a raised (ombrotrophic) peat bog. Signals from peat
342 sediment are expected to record mostly atmospheric inputs (solely rain), versus lake sediment from
343 the current study which include both terrestrial sediment (from runoff) and atmospheric inputs
344 (e.g. Fagel et al., 2014, Thevenon et al., 2011).

345

346 **4.2 Changes in Lead Sources Over Time**

347 **4.2.1 Anthropogenic Sources**

348 Lead isotopic data processed using FRUITS, a Bayesian mixing model, quantified the
349 importance of anthropogenic Pb inputs for each depth sampled (Fig. 4). Climatic periods included
350 in bars below both graphs present cold periods as blue bars, and warm periods as red bars. Arrows
351 along the top of Figure 4 indicate the building of a Teutonic Order fort (A.D. 1234; Urban, 1980)

352 and castle (late 13th century; Urban, 1980) at Radzyń Chełmiński; this activity would not have
353 impacted Rywałd.

354 Modeled anthropogenic Pb contribution is described from oldest to most recent inputs (Fig.
355 4). At Radzyń Chełmiński, the fraction of total lead attributed to anthropogenic inputs in the oldest
356 sediments appears to be influenced by anthropogenic Pb pollution from A.D. 883±99 to A.D.
357 1054±104. Contribution of Southwest Poland coal, ore, and slag during that period reaches a
358 maximum of 35% at A.D. 979±97. The anthropogenic fraction of total Pb remains below 1% from
359 A.D. 1168±114 to with A.D. 1296±94, then increases from the beginning of the 14th century
360 towards a dominantly anthropogenic contribution at the top of the core (up to 65%).

361 At Rywałd, the modeled anthropogenic contribution increases from the core bottom to
362 reach a maximum in A.D. 973±80 of 65%, and decrease to 1% at A.D. 1223±45. Subsequently,
363 the contribution sharply increases to 49% in A.D. 1303±54 and remains relatively stable with an
364 average value of 38±8% to the top of the core, with the exceptions of the two most recent samples
365 (74 and 86%).

366

367 **4.2.2 Mining Activity – Long Range Transport**

368 Atmospheric anthropogenic Pb signatures are expected to have been transported from
369 regional mines. Approximately 400 km to the south of Radzyń Chełmiński and Rywałd, in the
370 Rudawy Janowickie Mountains of Southwest Poland, a series of mines were active periodically
371 over the last millennium (e.g. Kierczak and Pietranik, 2011). Primary ores from Southwest Poland
372 include bituminous and brown coal, Cu, Zn, and Pb ores, native S, and rock salt (Rybicka, 1996).
373 Samples from Janowice, Wielkie, Szklary, Legnica, Miedzianka, and Wałbrzych sites in

374 Southwest Poland were used to represent an anthropogenic contribution (Fig. 4; Tyszka et al.,
375 2012). These mines are the nearest likely source of anthropogenic Pb in sediments from both
376 Radzyń Chełmiński and Rywałd. Documentation and precise dates are scarce prior to the 1800s,
377 but evidence can be pieced together through the few historical records available and archaeological
378 evidence.

379 First known Zn-Pb ore exploitation in Southwest Poland began in the Cracow-Silesia
380 district during the 12th to 13th centuries (Cabala et al., 2013). Mining and smelting of Cu in the
381 Rudawy Janowickie Mountains has occurred from the 14th century to present (e.g. Bukowski,
382 2011, Kierczak et al., 2013). Miedzianka, in particular was the largest center of mining and
383 smelting Cu, As, and Ag in Silesia, beginning as early as A.D. 1310 (Kierczak and Pietranik,
384 2011). These mining activities are probably responsible for the change in Pb isotopic ratios
385 observed at Rywałd just after A.D. 1200 (Fig. 4). Copper slags were deposited in the mountains
386 from the 14th to 16th century (Kierczak et al., 2013). Exploitation peaked in the 16th century, when
387 resources were exhausted, declining until the end of the 17th century (Kierczak and Pietranik,
388 2011). Our data indicates that this historical record of mining activity resulted in lead pollution
389 throughout the region, as shown by the relatively stable anthropogenic contribution in Rywałd for
390 the same time period followed by a small decrease. Ore mining activities became prevalent again
391 from the beginning of the 18th century to the beginning of the 19th century, focusing on Cu-rich
392 ore, as anthropogenic Pb again increases at Rywałd. Mining and smelting in the Rudawy
393 Janowickie mountains ceased entirely in A.D. 1925 (Kierczak and Pietranik, 2011, Kierczak et al.,
394 2013).

395 Coal exploitation was also prevalent in the Rudawy Janowickie Mountains of Southwest
396 Poland from the 12th century onwards, including two key basins, the Upper Silesian Coal Basin

397 (Bukowski, 2011, Rybicka, 1996) and the Lower Silesian Coal Basin (LSCB; Rybicka, 1996). Ore
398 was also mined in these basins. In Bytom and Olkusz, sub districts of the Upper Silesian Coal
399 Basin, Pb, Zn, and Cd ores were mined since the 12th-14th century (depending on source;
400 Ciarkowska et al., 2016, Rybicka, 1996,).

401 Additionally, from the 1800s onwards, anthropogenic contributions from modern mining,
402 bituminous coal combustion, and leaded gasoline exerted substantial control of the sedimentary
403 Pb isotopic compositions and concentrations at both sites, as documented in previous studies (e.g.
404 De Vleeschouwer et al., 2009b, Fialkiewicz-Koziel et al., 2018).

405 To test our hypothesis, a simple mass-balance calculation was applied. At Radzyn by
406 considering only the first 60 cm with a bulk density of approximately 1000 kg/m³, where a mean
407 increase in total Pb of about 5-10 ppm above baseline values can be observed, and by simplifying
408 the time required to accumulate these sediments to 1000 years, we can estimate an average
409 deposition rate of 3-6 mg.m⁻².y⁻¹. Considering this range of deposition rate, we cannot exclude
410 influences from other sources either local or distant.

411

412 **4.2.3 Land Use within Castle Lake Watershed – Short Range Transport**

413 Earliest palynological records at Radzyń Chełmiński suggest the region was dominated by
414 woodland with evidence of local small-scale agricultural activities present around A.D. 0-700
415 (Brown et al., 2015). The Wielbark culture was present in the area from the 2nd to the 5th century
416 A.D., during the Migration period (A.D. 300 to 700). The 5th to 9th century is marked by
417 archaeological evidence of tumuli and stone graves in the forest surrounding Radzyń Chełmiński,
418 with remains of a Slavonic settlement adjacent to the forest (Samojlik et al., 2013). There is also

419 archaeological evidence of depopulation from the 4th century until Slavic settlement from the 7th
420 century (Buko, 2008). A Slavic stronghold was constructed in proximity to Castle Lake around the
421 late 9th century (e.g. Urban, 1980).

422 Prior to Teutonic settlement, the land surrounding Castle Lake at Radzyń Chełmiński was
423 controlled by a Slavic Stronghold, occupied from the late 9th to mid 12th century when it may have
424 been burnt down in an attack (Brown et al., 2015, Chudziak, 1994). Concurrently, there was an
425 intensification in agricultural activity and decrease in woodland, causing increased soil erosion
426 into the surrounding wetland, as presented by palynological evidence (Brown et al., 2015;
427 Chudziak, 1996). Such erosion and increased land-use may have contributed to a decrease in
428 recorded anthropogenic contribution and Pb concentration at Radzyń Chełmiński. Palynological
429 evidence describes an increasingly open landscape in the pre-Crusading period (11th to 12th
430 century) of both intensifying arable and pastoral activity, with woodland retained on nearby land
431 (Brown et al., 2015).

432 Teutonic influence is documented at the location from A.D. 1234 to around A.D. 1454
433 when the Order ceded the territory to Polish control (Pluskowski, 2013; Urban, 1980). The
434 Crusading period began in A.D. 1230, concurrent with the founding of the Teutonic Order castle
435 and town at Radzyń Chełmiński (Brown et al., 2015). During this period agricultural and pastoral
436 land-use was relatively stable surrounding the Castle Lake (Brown et al., 2015). A timber fort was
437 constructed in A.D. 1234, and the castle was later built between A.D. 1310 and 1340 (e.g. Brown
438 et al., 2015). Previously published palynological evidence from Radzyń Chełmiński recorded
439 changes in vegetation and land use during this period, including a decrease in arboreal pollen and
440 increase in cereal pollen (Brown and Pluskowski, 2011; Pluskowski, 2013). The period between
441 A.D. 1350 and 1400 is known as the “Golden Age” of Teutonic Order influence (e.g. Pluskowski,

442 2013). Heathland developed along with agricultural intensification from the late 14th to 15th
443 century, accompanied by a decrease in woodland area (Brown and Pluskowski, 2011). In addition
444 to landscape changes with the arrival of the Teutonic Order, trade routes also developed by efforts
445 to exploit Prussian resources, adding to human impact from the nearby settlements (Harte and
446 Ponting, 1983). As the frontier land between Teutonic Order Prussia and Poland, the Chełmo land
447 (Kulmerland in German), including Radzyń Chełmiński and Rywałd experienced intermittent
448 raids from Prussian tribes, including the Great Prussian Uprising of the 1260s, and subsequent
449 transformation of the landscape (Lukowski and Zawadzki, 2001; Pluskowski, 2013). Such
450 agricultural intensification and castle building may have contributed to altered the regional
451 anthropogenic isotopic signal from the opening of mines within the sediment records, minimizing
452 the expected increase in anthropogenic Pb contribution that was detected at Rywałd, while at the
453 same time causing an increase in Pb concentration.

454 In A.D. 1410, Radzyń Chełmiński Castle was damaged by Polish-Lithuanians (e.g.
455 Pluskowski, 2013). From A.D. 1412 to 1439, the surrounding landscape was subjected to multiple
456 seasons of crop failure, causing many villages in the area to be covered by woodland by A.D. 1444.
457 The Thirteen Years war occurred shortly after, from A.D. 1453 to 1466, with many conflicts
458 occurring near Radzyń, after which the castle became occupied by Poland (e.g. Pluskowski, 2013),
459 falling into ruin by the 16th century (Brown et al., 2015). Further damage occurred during the
460 Swedish Invasion from A.D. 1626 to 1629 (e.g. Brown et al., 2015). Wooded areas contribute
461 minimal weathered and eroded sediment to the surrounding basin, compared to predominantly
462 open fields (arable and pastoral land). The decrease in local influence from the nearby castle and
463 town, and re-establishment of woodlands, may have allowed for a return to a predominantly
464 regional, atmospheric Pb-derived signal in the sediment record during this period.

465

466 **4.2.4 Regional Climatic Influence**

467 Differentiating between climatic and historical influences remains challenging. Although
468 Pb isotopes are not climate proxies, it is possible climate change or influencing meteorological
469 conditions (e.g. change in dominant wind direction patterns, increase in rainfall, flood events, etc.)
470 might indirectly influence Pb isotopic signatures by promoting the development of human
471 activities (e.g. Büntgen et al., 2016, 2011), mostly during warmer and dryer periods. According to
472 our sediment data (SI_2, SI_3), the Radzyń Chełmiński core is made entirely of lake
473 mud/sediment; while Rywałd contains peat sediment from 0 to 68 cm, and lake mud/sediment
474 from 68 cm to the bottom of the core.

475 Sedimentary records for both cores span five climatic periods: 1) Late Antique Little Ice
476 Age (LALIA, A.D. 536 to 660; e.g. Berglund et al., 2003; Büntgen et al., 2016); 2) the Climatic
477 Optimum in Prussia (COP, A.D. 800 to 1150; e.g. Pluskowski, 2013); 3) the Medieval Warm
478 Period (MWP; A.D. 800 to 1300; e.g. De Vleeschouwer et al., 2009b); 4) the Little Ice Age (LIA;
479 A.D. 1300 to 1850; e.g. De Vleeschouwer et al., 2009b; Hegerl et al., 2017; Lockwood, 2001);
480 and 5) Global Warming (GW; A.D. 1890 to present; e.g. Chiriloaei et al., 2012; Hegerl et al.,
481 2017). Unlike in Western Europe, Prussian communities did not experience a regression after the
482 medieval warm period, and instead thrived (Pluskowski, 2013). We hypothesize that promotion of
483 human activities during favorable climatic conditions (Büntgen et al., 2016) included behaviors
484 that mobilize lead, such as coal burning and ore utilization.

485

486 **5. CONCLUSION**

487 In this study, Pb concentrations and isotope ratios were used to quantify anthropogenic lead
488 inputs and sources, as well as to identify trends in human activity in Northern Poland over the last
489 1,500 years. The use of a rural lake sediment core at Rywałd and a lake core influenced by a nearby
490 town and Teutonic Order castle at Radzyń Chełmiński enabled differentiation between local and
491 regional anthropogenic inputs.

492 Two primary Pb sources have been identified: (1) coal, ore, and slag originated from
493 Southwestern Poland mining activities (long range transport); and (2) erosion from the surrounding
494 watershed associated with the development of human activities (short range transport). High
495 anthropogenic Pb contributions from the 9th to 11th centuries A.D., in the absence of historical
496 evidence for mining activity in Southwestern Poland, point to a previously-unrecognized,
497 substantial anthropogenic pb source during that time period. Local activities dominated the Pb
498 isotopic record from the 11th to 13th centuries A.D., during periods of Slavic and subsequent
499 Teutonic Order settlement and castle building, and agricultural intensification. The long range,
500 anthropogenic, mining signal was elevated around the 16th and 18th to 19th centuries A.D., during
501 periods of decreased local human agricultural activity.

502 Overall, the sediments at Rywałd recorded mostly long range mining inputs originating
503 from Southwest Poland, while Radzyń Chełmiński sediments recorded both sources long range
504 mining signal and local signal from an increase in agricultural and other human activities related
505 to the development of the town and castle. Further studies are required to identify the sources
506 responsible for the anthropogenic signal observed for our sites prior to A.D. 1000.

507

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515

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Figure
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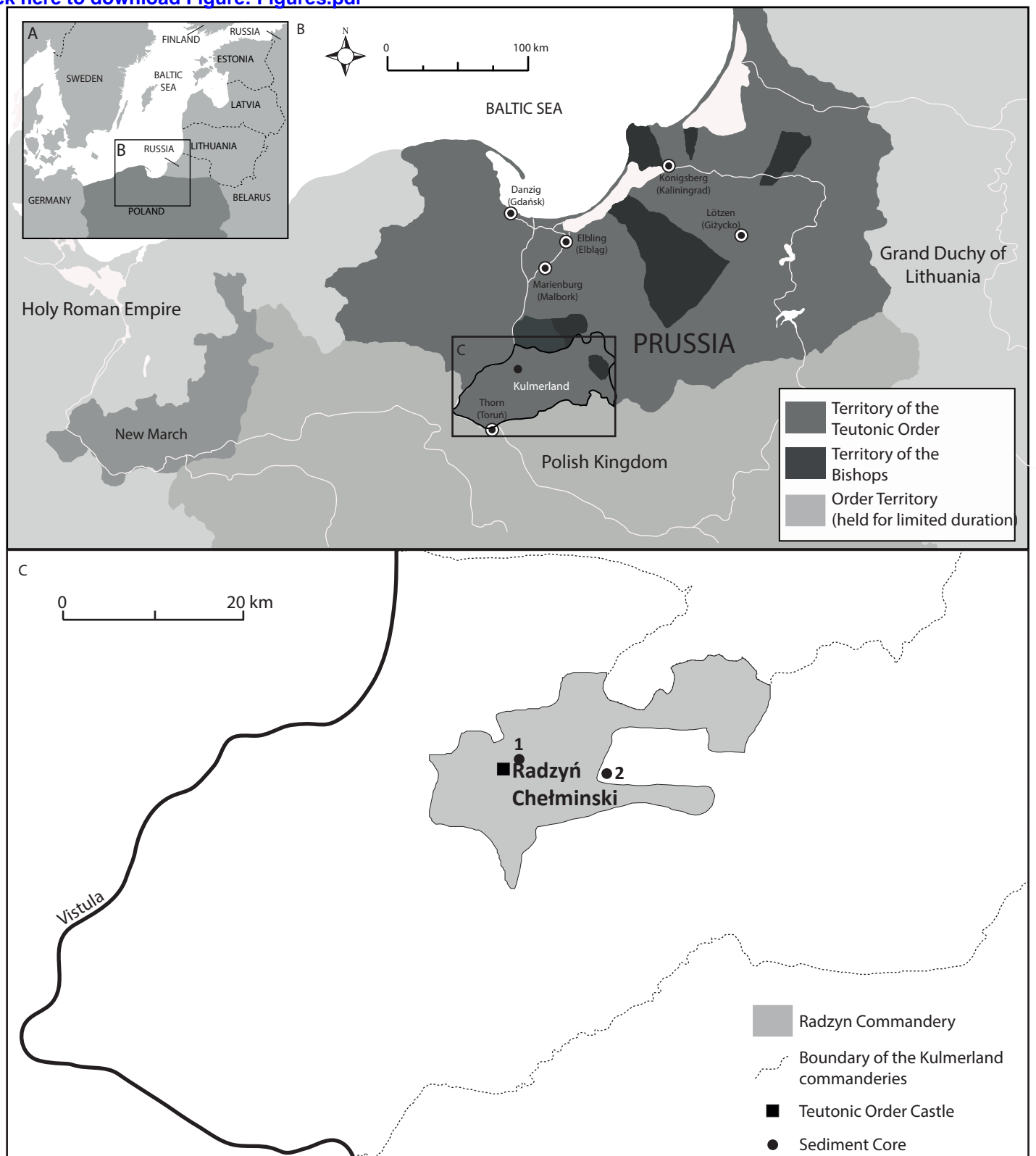


Figure 1

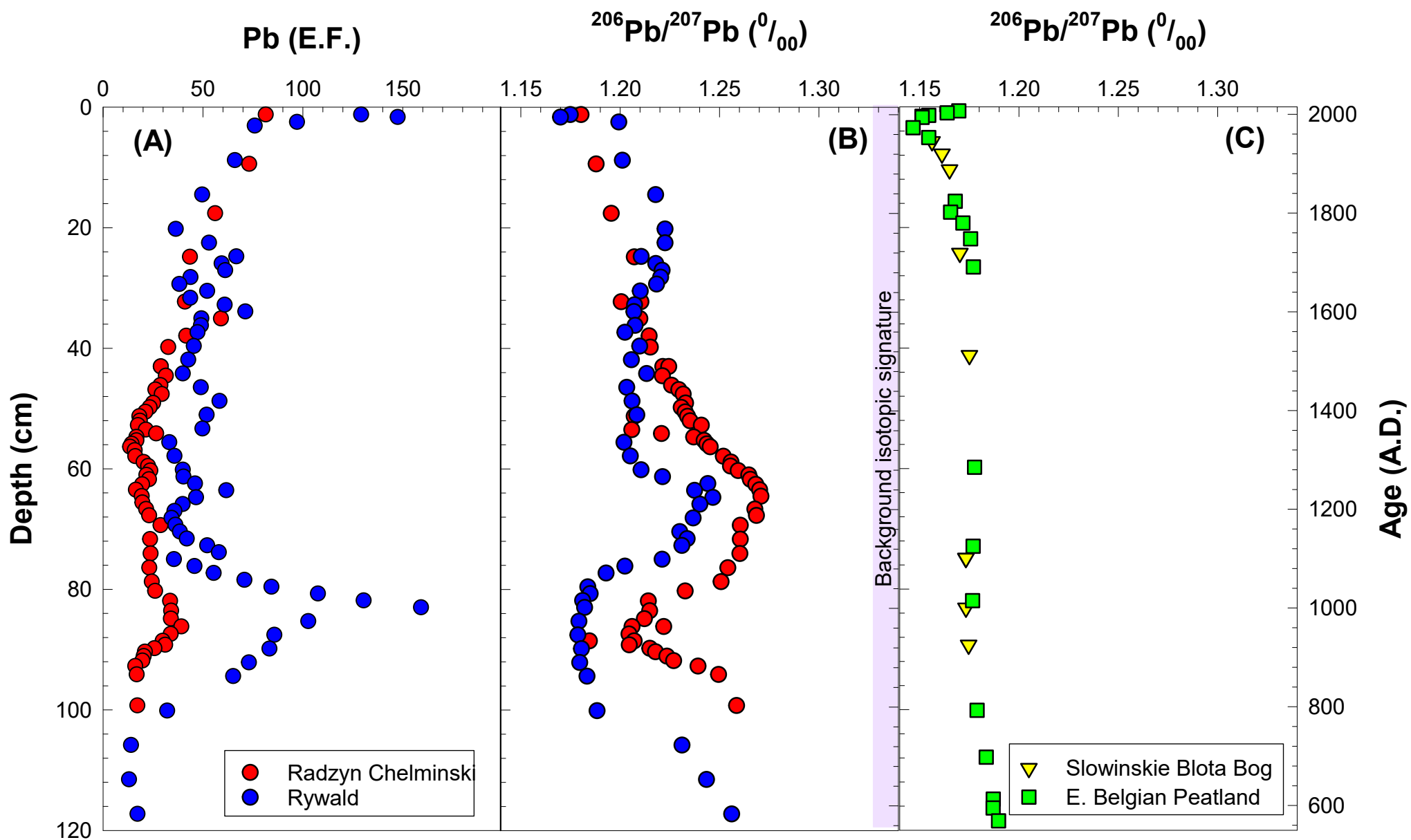


Figure 2

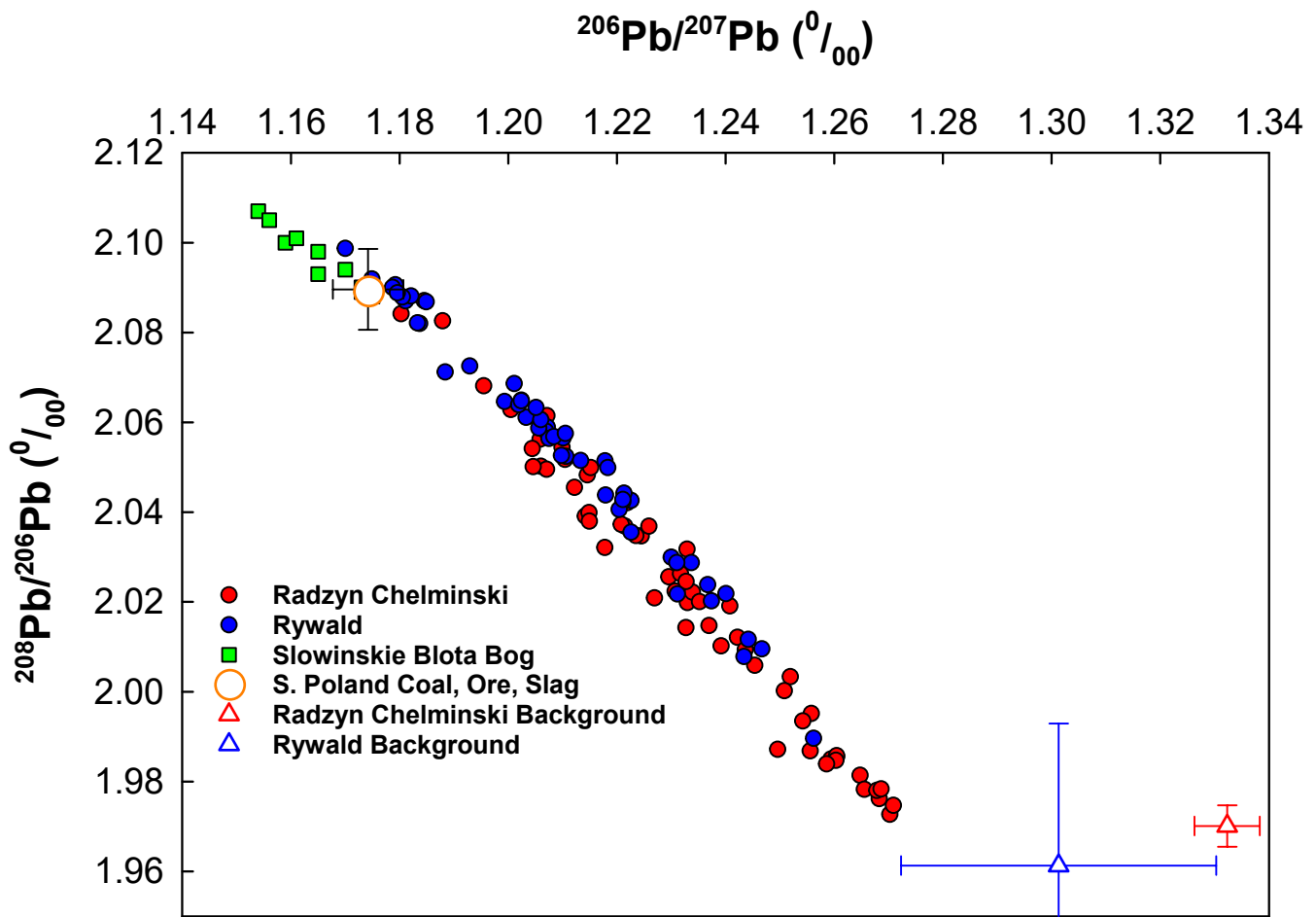


Figure 3

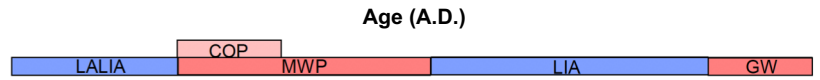
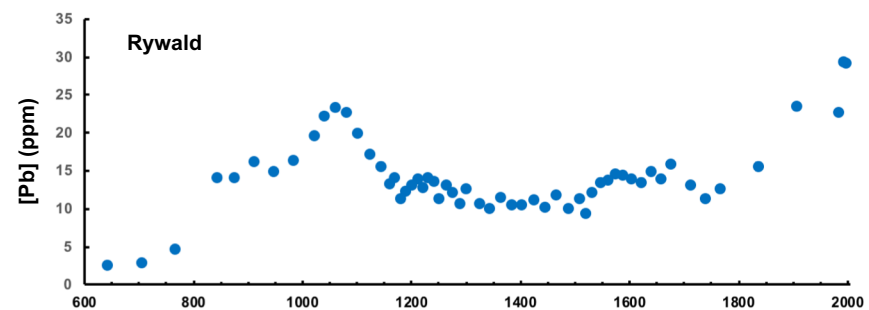
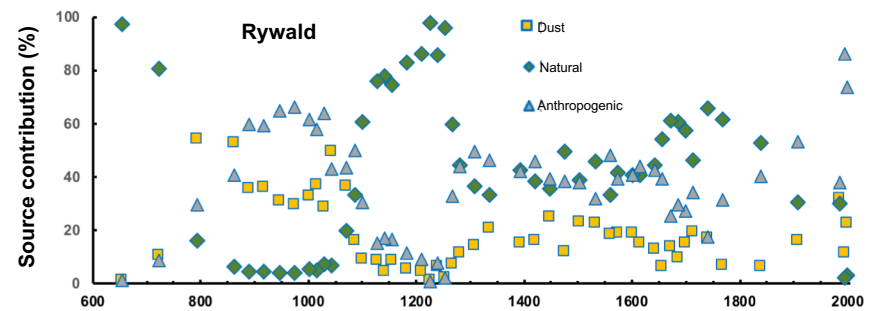
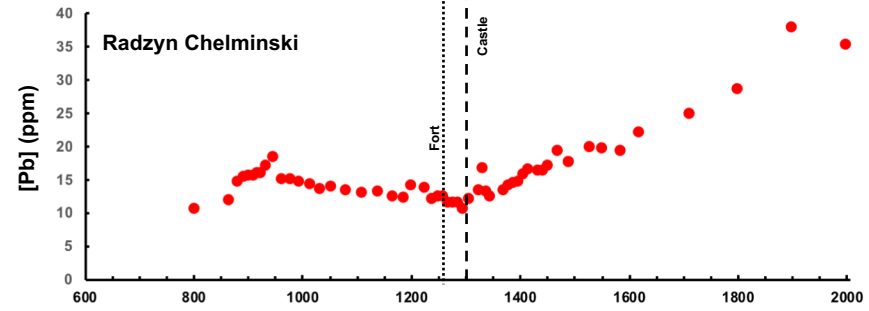
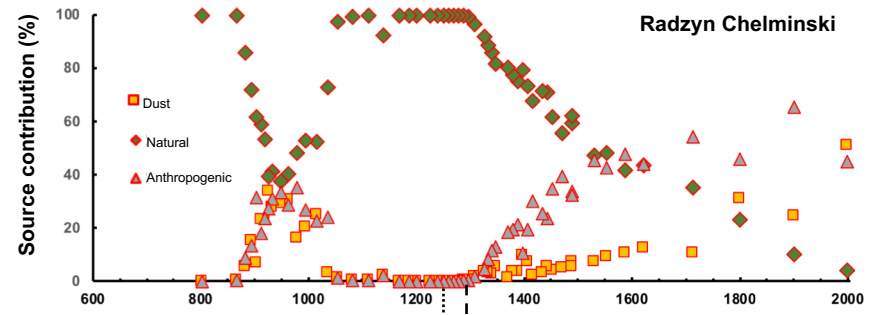


Figure captions

Figure 1: Site Map. A) Central and Eastern Europe, B) Location of the Kulmerland within Medieval Prussia, including lands controlled by the Teutonic Order, C) The Kulmerland region including (1) Radzyń Chełmiński core, Radzyń Chełmiński Castle, and (2) Rywałd core (modified from Brown et al., 2015).

Figure 2: Sedimentary profiles of Pb enrichment factors (E.F., left panel), $^{206}\text{Pb}/^{207}\text{Pb}$ (‰) isotopic ratios for Radzyń Chełmiński and Rywałd (middle panel, the vertical light purple represents the $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic signature of the background, i.e. underneath earth material layer), and previously published profiles (right panel) from a bog located in Northern Poland (De Vleeschower et al., 2009) and a Belgian Peatland (Fagel et al., 2014).

Figure 3: $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic ratio three-point plot. Red dots, blue dots, green squares, open orange circle, open red triangle and open blue triangle represent Radzyń Chełmiński, Rywałd, Slowinskie Blota Bog (De Vleeschower et al., 2009), Poland ore, slag, coal (Tyszka et al., 2012), Radzyń Chełmiński background and Rywałd background, respectively.

Figure 4: Source contribution -dust, natural and anthropogenic-(top panel for Radzyń Chełmiński and third panel for Rywałd) and Pb concentration (second panel for Radzyń Chełmiński and bottom panel for Rywałd) versus time (horizontal bottom axis). Source contribution was calculated

using a Bayesian code (FRUITS) using $^{206}\text{Pb}/^{207}\text{Pb}$ ‰ and $^{208}\text{Pb}/^{206}\text{Pb}$ ‰. See main text for detailed explanation about the modeling. Horizontal bars (blue and red) below the plot displays climatic periods. Late Antique Little Ice Age (LALIA, 536 to 660 AD; left blue bar). Climatic Optimum in Prussia (COP, 800 to 1150 AD; light red bar on the top). Medieval Warm Period (MWP; 800 to 1300 AD; left red bar). Little Ice Age (LIA; 1300 to 1850 AD; right blue bar). Global Warming (GW; 1890 to present; right red bar). Vertical arrows are only relevant to Radzyń Chełmiński and represent the Teutonic timber fort built (1234 AD; Urban, 1980) and the Radzyń Chełmiński Castle Built (late 13th century; Urban, 1980), respectively.

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