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MERCURY IN THE SEDIMENTS OF SELECTED PEATLANDS IN MAŁOPOLSKA REGION

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Abstract. The mercury content in peat layers of seven peat bogs in the Małopolska region (Wolbrom in the Kraków-Częstochowa Upland and Otrębowskie Brzegi, Puścizna Wysoka, Puścizna Mała, Przybojec, Puścizna Długopole and Bór na Czerwonem in the Orawa-Nowy Targ Basin) was determined to a depth of 100 cm at a resolution of 1–2 cm. Geochemical background and level of anthropogenic mercury enrichment were determined for each peat bog. To establish the interdependence between mercury concentration, mineral matter content and selected metals, geochemical diagrams and models of the system were drawn up representing the correlational relationships between the selected geochemical variables for three of the peat bogs in the Orawa--Nowy Targ Basin (Otrębowskie Brzegi, Przybojec and Bór na Czerwonem). It was found that, comparing against other European raised bogs, the range of mercury concentrations in the peat layer down to 50 cm in the peatlands of Małopolska is similar to those in Norway, Sweden, Denmark and Spain, and decidedly lower than in the peatlands in Scotland, Belgium and Czechia. Furthermore, the sites in the Orawa-Nowy Targ Basin were clearly lower, the lower the altitude of the peat bog surface, which is probably associated with local topoclimatic conditions.

Key words: raised bog, geochemistry, heavy metals, human impact, southern Poland

Introduction

Mercury is a metal that has been in human use for ~2400 years, both in its pure form and as mercury sulphide HgS, i.e. cinnabar (Eichstaedt 1970). Since Roman times, mercury has been used in obtaining gold and silver from river sands, while powdered cinnabar was used tomake red dye. The toxic and healing properties of mercury alike have long been known (Kłys 2010). Already in the 11th century, mercury vapour was being used in Chinese medicine (Szumowski 1935), and combinations of mercury and various substances were used much earlier in cosmetics. Thanks to Paracelsus, this metal began to be used to treat poorly healing wounds, ulcerations and syphilis (Szumowski 1935; Eichstaedt 1970; Kłys 2010).

Mercury is among the elements that are highly dispersed in the lithosphere, where its content rarely exceeds a few hundredths of a milligram per kilogramme (Alloway, Ayres 1997). It accumulates mainly in the surface layer of clay and peat soils by binding with humus, sulphur and clay minerals (Kabata-Pendias, Pendias 1993; Migaszewski, Gałuszka 2007).

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Palaeogeographic studies show that the greatest amounts of mercury were introduced into the natural environment – and particularly into the atmosphere – around the mid-20th century. This is reflected in the metal's content not only in bog sediments (Benoit *et al.* 1998; Martinez-Cortizas *et al.* 1999; Roos-Barraclough *et al.* 2002; Biester *et al.* 2002, 2006; Steinnes, Sjøbakk 2005; Farmer *et al.* 2009; Zaccone *et al.* 2009; Rydberg *et al.* 2010; Zuna *et al.* 2012; Allan *et al.* 2013; Coufalík *et al.* 2013; Küttner *et al.* 2014; Talbot *et al.* 2017) but also in lacustrine sediments (Lockhart *et al.* 1998; Santos *et al.* 2001; Cannon *et al.* 2003; Ribeiro-Guevara *et al.* 2010; Thevenon *et al.* 2011; Hermanns, Biester 2013; Lacerda *et al.* 2017; Schütze *et al.* 2018; Guédron *et al.* 2019; Péres-Rodrígues *et al.* 2019; Okupny *et al.* 2020; Juśkiewicz, Gierszewski 2022) and marine sediments (Hare *et al.* 2010; Leipe *et al.* 2013; Ignatavičius *et al.* 2022).

Because mercury migrates mainly through the atmosphere (Mason *et al.* 1994), it also occurs in the sediments of raised bogs, these being fed mainly by precipitation (Roos-Barraclough *et al.* 2002; Farmer *et al.* 2009; Zaccone *et al.* 2009; Zuna *et al.* 2012; Allan *et al.* 2013; Coufalík 2013).

Mercury is toxic to both animals and plants, even at very low concentrations. Plants take it not only from the soil, but also directly from the air. This mechanism is indicated by mercury concentrations being much higher in non-vascular plants, especially mosses and lichens (Hall, St Louis 2004; Wojtuń *et al.* 2013; Olson *et al.* 2019).

In recent years, attention has been drawn to the fact that elemental mercury (Hg°) is more readily absorbed by plants in colder climates. This was first reported by Martinez-Cortizas *et al*. (1999, 2007) and confirmed in later works (Bargagli 2016; Obrist *et al.* 2017; Jiskra *et al.* 2018; Olson *et al.* 2018; Li *et al.* 2020).

The mercury content of raised bog sediments in Poland is very poorly known. To date, mercury concentrations have been determined for only a few bogs of this type, namely in Otalżyno in the Kashubian Lake District (Bojakowska, Tołkanowicz 2015), in Radacz, Gryfice, Reptowo and Chłopowo in Western Pomerania and Lipskie Bagno in Wielkopolska (Miszczak *et al.* 2020). In all three cases, these were survey studies determining trace element concentrations, including for mercury, in peat samples for core sections of 5–15 cm long. The aim of this article is to present the stratigraphic variability and spatial differentiation of total mercury content in the sediments of selected peat bogs of the Małopolska region (down to a depth of 1 m, at a resolution of 1–2 cm), including the raised bog environment's degree of anthropogenic mercury contamination.

Study area

The study area is located in southern Poland (Fig. 1A), and more precisely in the northern and southern parts of Małopolska region, where transitional and raised bogs exceed 40% of the total number of bogs (Fig. 1B). Because the raised bogs are fed by rainwater only and thus offer the possibility of recording historical and present-day metal deposition in peat sediments, it should be noted that combustion of fossil fuels may account for as much as 69% of anthropogenic mercury (Pacyna, Pacyna 2001). This is very important, as the mercury content in the coal of some Upper Silesia mines is as high as 0.76 mg/kg (Bojakowska, Sokołowska 2001). As a result, the concentrations of mercury in soils and water sediments ofthis region are several times higher than the regional geochemical background level (Pasieczna 2012, 2014; Baran *et al.* 2015).

Within the study, seven research sites were selected for determination of mercury content in bog sediments of the Małopolska region (Fig. 2, 3; tab. 1). One, the Wolbrom site, is located in the Kraków-Częstochowa Upland, while the others are all in the Orawa-Nowy Targ Basin. The two research sites lie east and south-east of the Upper Silesian Industrial District, where the density of mercury emitters to the environment is currently the highest in the country, accounting for a total in the range of 24–54 kg/year (Zyśk *et al.* 2011), whereas the local geochemical background is at 0.05–0.11 mg/kg (Pasieczna 2012; Fig. 1C). In addition, the study area is exposed to the negative effects of the mining and processing of Pb, Zn, Cu, Cd, Cr and Ni ores (Pasieczna 2008; Cabała 2009; Koncewicz-Baran, Gondek 2010).

Table 1

Description of research sites

Name of study site	Location of cores		Altitude of core location (m a.s.l.)	Area of the peatland (ha)	
	φ	λ		total	raised bog
Wolbrom	50° 22' 40 "	19° 46' 35"	~375	~80	~40*
Otrębowskie Brzegi	49° 27' 45 "	19° 39' 27"	~605	56,2	8,8
Puścizna Wysoka	49° 24' 47 "	19° 43' 34"	~692	48,2	3,2
Puścizna Mała	49° 27' 31 "	19° 47' 30"	~660	108,8	51,2
Przybojec	49° 23' 30 "	19° 47' 32"	~769	140,0	96,2
Puścizna Długopole	49° 27' 42 "	19° 54' 38"	~634	161,2	43,8
Bór na Czerwonem	49° 27' 35 "	20° 02' 29"	~618	66,8	30,5

*presumed area of former dome before draining of the peat bog

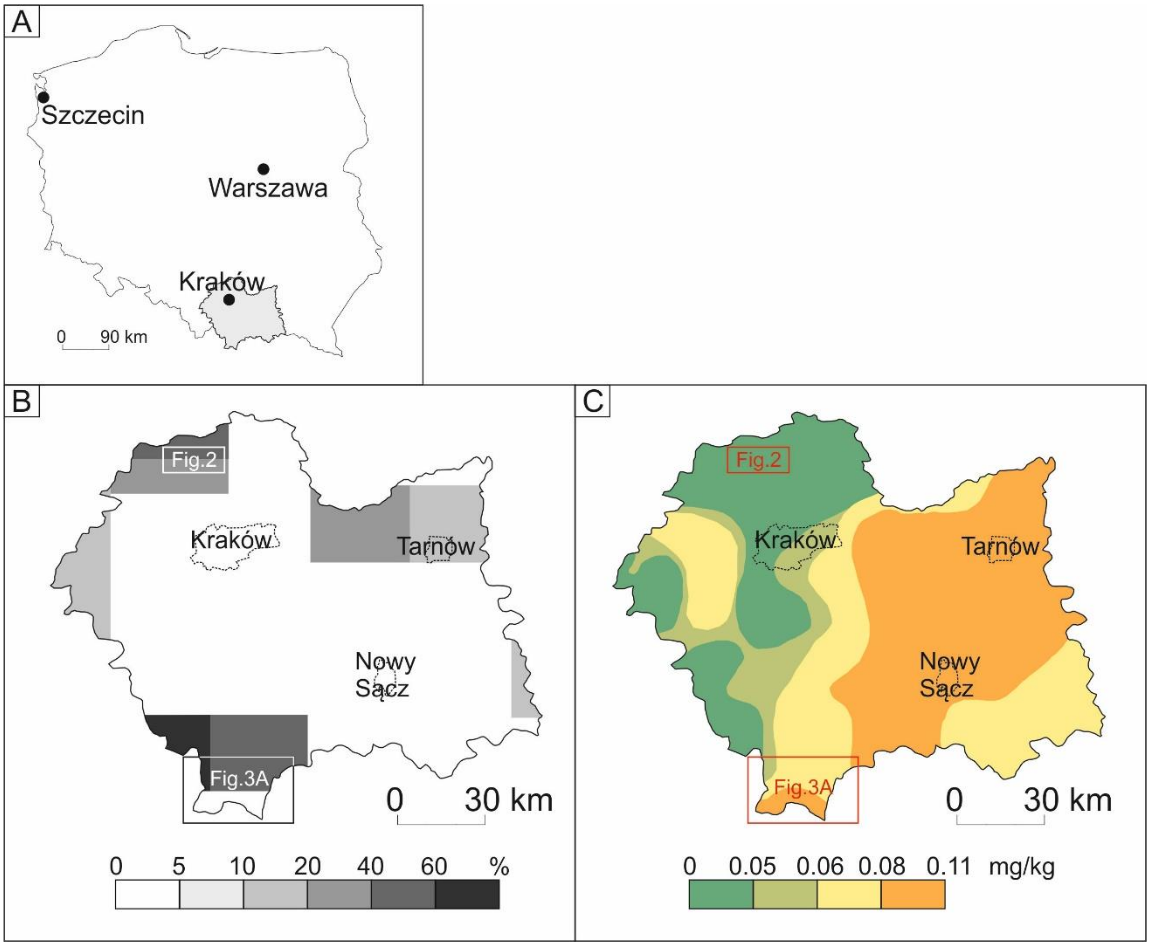

Fig. 1. A – Location of the study area in Poland
B – against the ratio (in %) of the number of deposits of raised bogs and transition bogs to the general number of eposits presented on a square network after Żurek (1987)
C – results of geochemical background Hg (in mg/kg) of soils in non-built-up areas after Pasieczna (2012)

The vicinity of Wolbrom lies within the so-called Wolbrom Gate (Fig. 2), a fairly wide depression that constitutes the border of the Częstochowa Plateau to the north and the Ojców Plateau to the south (Gilewska 1972). The peat bog itself currently lies within the Wolbrom city limits, in the south-east of the city at an altitude of ~375 m a.s.l. It is a watershed peatland constituting the source of two small rivers – the Pokrzywianka, which is part of the Biała Przemsza catchment, and the Szreniawa, which flows directly into the Vistula. It occurs in the Wolbrom Trench zone (Górka,

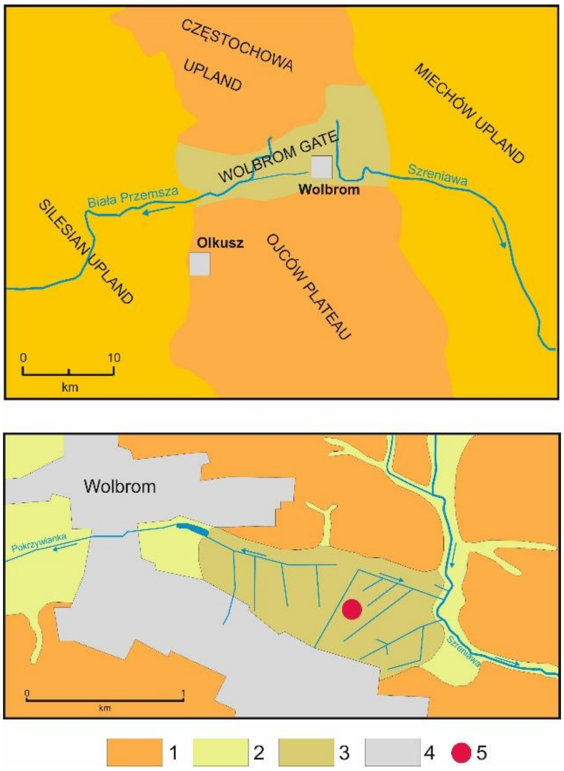

Fig. 2. Localisation of Wolbrom peatland against physico-geographical units of Małopolska Upland after Gilewska (1972) division
1 – area of the plateau, 2 – bottom of the river valley, 3 – peatlands, 4 – urban areas, 5 – location of the Wolbrom core

Pasternak 2021) and fills a fossil depression of unclear origin (karst?), developed within Upper Oxford plate limestones (Wolbrom limestones).

In the Wolbrom region, the average annual air temperature is ~7ºC, with monthly averages ranging from –3ºC in January to 17.5ºC in July. The annual sum of precipitation is usually between 650 and 750 mm.

The studies of Obidowicz (1976) show that the bog basin contains several depressions whose organic sediments are up to five metres thick. About 100 years ago, despite being significantly degraded by peat extraction, a raised bog developed here (Trela 1928). At that time, plant species typical of raised bogs were common in the area (Kozłowska 1923). However, 50 years later, the bog was found to be in a state of advanced and rapidly progressing anthropogenic degradation that had been initiated by the water relations being disturbed by the network of drainage ditches built around 1942 and by its subsequent afforestation (Michalik *vide* Latałowa 1976). Palynological and chronostratigraphic studies have shown that peat sedentation lasted from the Older Dryas to modern times here, with a clear break in the Subboreal (Latałowa 1976; Latałowa, Nalepka 1987). The latest radiocarbon datings of the top layer of bog sediments from the W3 profile (Pawełczyk *et al.* 2017, 2018) show undisturbed peat sedentation in the age range of 5000–150 BC, i.e. from a depth of 105 to 40 cm, whereas the radiocarbon age of the peat samples is ambiguous above 40 cm but, in conjunction with ^{210}Pb age determinations, indicates a hiatus in AD ~750 to ~1850.

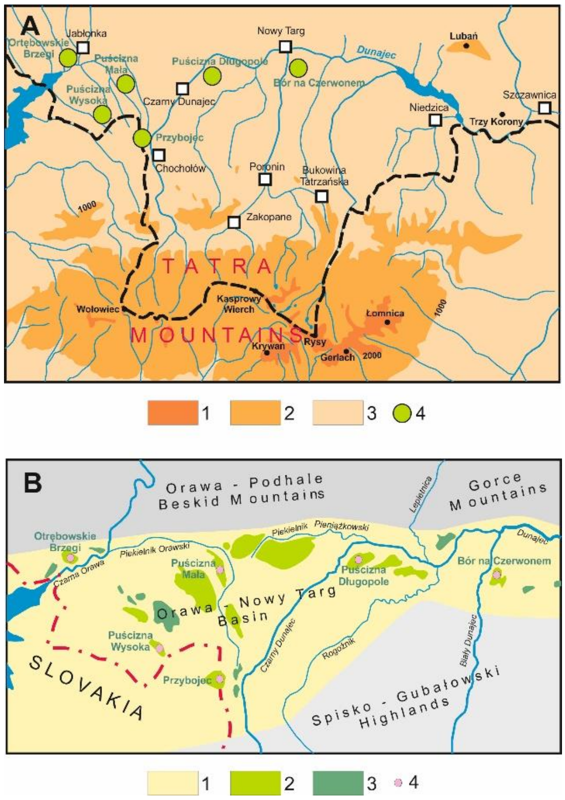

Fig. 3. Localisation of peatlands in the Orawa-Nowy Targ Basin after Łajczak (2009)
A: 1 – areas with an altitude of more than 2000 m a.s.l., 2 – areas ith an altitude between 1000-2000 m a.s.l., 3 – areas with an altitude of 500-1000 m a.s.l., 4 – location of the research raised bog
B: 1 – Orawa-Nowy Targ Basin, 2 – raised bogs, 3 – fen peatlands, 4 – location of the research cores

The Orawa-Nowy Targ Basin hosts several tens of peat bogs of various sizes and origins (Łajczak 2006, 2009). It is an east–west-oriented inter-mountain valley bounded to the north by belts of the Western Beskids (the Orawa-Podhale Beskid to the west and the Gorce Mountains to the east) and to the south by the Spisko-Gubałowski Highlands together with the Pieniny Klippen Belt (Fig. 3).

This depression is drained to the west and southwest by the Czarna Orawa river, which belongs to the Danube catchment, and to the east by the Dunajec, a tributary of the Vistula. Thus, the basin is bisected by the European watershed separating the Black Sea and Baltic Sea catchment areas.

The Orawa-Nowy Targ Basin has a moderately cool climate with an average annual air temperature of 4–6°C (Hess 1965). The average sum of precipitation here ranges from 700 to 900 mm, with the maximum precipitation falling in the summer (Hess 1965; Łupikasza *et al.* 2016). In winter seasons, under high-pressure conditions, pools of cold air form in the valley, causing haze and temperature inversions, as well as smog (Łabij-Reduta *et al.* 2019). Measurements show that Nowy Targ has the highest number of smog days per year (90 days in 2020) of any town in Poland, as well as the highest annual concentration of PM_{10} and $PM_{2.5}$ particulate matter (Jędruszkiewicz *et al.* 2016, 2017).

The following six raised bogs of this region were selected for mercury content in their bog sediments: Otrębowskie Brzegi, Puścizna Wysoka, Puścizna Mała, Przybojec, Puścizna Długopole and Bór na Czerwonem (Fig. 3; tab. 1). Peat sediment cores were collected from the central part of the dome of each peat bog.

The Otrębowskie Brzegi peat bog is located in the west of the Orawa-Nowy Targ Basin on a post-glacial, over-flood terrace of the Czarna Orawa, at ~605 m a.s.l. The bog sediments here reaches a maximum thickness of ~3 m (Pawełczyk *et al.* 2019) and began to accumulate Atlantic Period, about 4 200 years BC (Pawełczyk *et al.* 2018).

The Puścizna Wysoka peat bog is located 2.5 km east of the village of Sołtysowo Wyżnie near Jabłonka, at ~690 m a.s.l. on a terrace formed during the glaciation of the Tatra Mountains in the Mindel Glacial Stage (Łajczak 2009). It is drained by small left tributaries of the Czarna Orawa (Chyżnik and Borcok). In the past, it was intensively exploited. During the 20th century (from 1994 to 2000), its total area decreased by ~55% and the dome itself by 90% (Łajczak 2001).

The Puścizna Mała peat bog is located ~3 km south-south-east of the village of Piekielnik in the Czarny Dunajec commune, at an altitude of ~660–665 m a.s.l. on a terrace associated with the Riss glaciation in the Tatra Mountains (Łajczak 2009). Currently, it is drained by numerous drainage ditches flowing into the Czarna Woda and Grunik – tributaries of the Piekielnik Orawski.

The Przybojec peat bog lies on the Polish–Slowak border, ~2 km west of the village of Koniówka (Czarny Dunajec commune). It occupies a watershed area at an altitude of 765–770 m a.s.l. between the Czarna Orawa and Czarny Dunajec river catchments. According to Łajczak (2001), during the 20th century, it decreased in area by ~34% and dome itself by 20%.

The Puścizna Długopole bog lies in the Czarny Dunajec catchment at 630–635 m a.s.l. It lies in a watershed position between the valleys of the Czarny Dunajec and its tributary, the Czarny Potok. During the 20th century, its total area decreased by ~12% and the area of the dome by ~25% (Łajczak 2001).

The peat bog, and indeed the Bór na Czerwonem nature reserve, is located within the administrative borders of Nowy Targ, ~2.5 km from the city centre. It lies at an altitude of ~615–620 m a.s.l. on a terrace created during the Weichselian glaciation of the Tatra Mountains. The raised bog was already protected in 1925 (Zając 2015). However, according to Łajczak's research (2001), since 1894, it has decreased in area by ~42% and the dome itself by 56%. The maximum thickness of the peat in the area of the dome is ~4.5–5 m, and palynological analysis shows that its accumulation began in the Atlantic Period (Obidowicz 1990).

Methods

In order to determine the mercury content in the sediments of the analysed peatlands of the Małopolska region, 1-m cores of surface sediments of undisturbed structure were collected using "INSTORF" samplers with a diameter of 6 or 10 cm (Fig. 4). Fresh cores were packed in PVC gutters, and, in laboratory conditions, individual core segments were divided into 1-cm slices to a depth of 50 cm and 2-cm slices from a depth of 50 to 100 cm. This produced 75 samples for mercury content analysis for each 1-m sediment core. In the Geochemical Laboratory of the Institute of Marine and Environmental Sciences of the University of Szczecin, samples were lyophilised using a Beta 1–8 LDplus laboratory freeze-dryer (manufactured by Martin Christ) and then homogenised in an agate mortar. The concentration of mercury (Hg) was determined on a DMA-80 Direct Mercury Analyser (by Milestone), in three replications per sample, from which the average content was then calculated.

Fig. 4. Puścizna Mała raised bog – upper 50 cm layer of peat sediments taken with the Instorf samples *(photo by J. Słowińska 2018)*

In addition, for the three profiles from the Otrębowskie Brzegi, Przybojec and Bór na Czerwonem peat bogs, the residue after roasting at 550ºC (ash content) was also determined, as were the concentrations of selected metals (K, Fe, Mn, Cu, Zn, Pb), according to an earlier described procedure (Borówka 1992; Mirosław-Grabowska *et al.* 2022) using a SOLAAR 969 atomic absorption spectrometer (by Unicam).

Results

At all analysed sites, the 100-cm-thick surface peat layer exhibited a very clear increase in mercury concentration, from values typical of natural environments to values indicating significant human impact (Fig. 5). Based on the analysis of changes in mercury content in the sediments of individual peat bogs, mercury concentrations are concluded to be at natural levels in all profiles below depths of 70 cm. The average concentration of Hg in the 70–100 cm depth range varies between profiles (tab. 2), reaching a maximum in the Otrębowskie Brzegi bog (30.1 µg/kg) and a minimum in the Przybojec bog (12.6 µg/kg). If the average Hg concentrations for the analysed profiles are considered to constitute the geochemical background, then, for each profile, the thickness of the peat layer with a clearly elevated mercury content (mainly due to human impact) can be determined (Fig. 5).

According to the measurements (tab. 2), the average mercury content was highest in the Wolbrom and Puścizna Długopole peat bogs, while it was decidedly lowest in the Przybojec bog. Absolute maximum mercury concentrations exceeding 300 µg/kg were found in a layer of polluted sediments at the following sites: Bór na Czerwonem (473 µg/kg), Otrębowskie Brzegi (379.5 µg/kg) and Puścizna Długopole (303.9 µg/kg). The variation in mercury content with depth clearly differs between sites (Fig. 5). In Wolbrom, the Hg content is high but stable (200–220 µg/kg) to a depth of 22 cm, with a maximum at the very surface (0–1 cm). In Otrębowskie Brzegi, the concentration of Hg gradually increases upwards from 40 to 13 cm deep to reach its maximum (379.5 µg/kg) before decreasing to 120–190 µg/kg in the surface layer. In the Puścizna Wysoka and Puścizna Mała bogs, the content of Hg increases rapidly from 30 to 20 cm deep – from 50 µg/kg to ~200–250 µg/kg, to then stay at this level almost to the very surface. Only in the 5–0-cm layer is it slightly lower. In the profile from the Przybojec mire, in the 40–0 cm layer, mercury content peaks twice – at 32 cm (61 µg/kg) and 13 cm (216 µg/kg). From the more shallow-lying peak, the concentration gradually decreases to 38 µg/kg at the very surface. In the Długopole bog, the mercury concentration starts to increase gradually from 60 cm deep up to 30 cm (304 µg/kg), after which it shows a decreasing trend to the surface, where it reaches ~70–95 µg/kg. In the Bór na Czerwonem peat bog, from a depth of 55 cm upwards there are two peaks in Hg content – at 30 cm (90 µg/kg) and 6 cm deep (473 µg/kg). Above this, the concentration drops slightly to 257 µg/kg.

To establish the interdependence between mercury concentration, mineral matter content and selected metals, geochemical diagrams were drawn up for the three sites at Otrębowskie Brzegi, Przybojec and Bór na Czerwonem. In the Otrębowskie Brzegi peat bog, the heavy metals differ slightly in terms of the depths at which their peaks occur (Fig. 6). The earliest and thus lowest peaks (at a depth of 12–13 cm) are for Hg content, but also for potassium and mineral matter. Slightly higher, at a depth of 8–9 cm, Pb concentration peaks, and, at a depth of 4–5 cm, Cu is at its highest concentration. By contrast, Zn has its maximum share only in the surface sample (0–1 cm). This situation results in a rather weak system of correlations between the analysed geochemical variables at the Otrębowskie Brzegi site

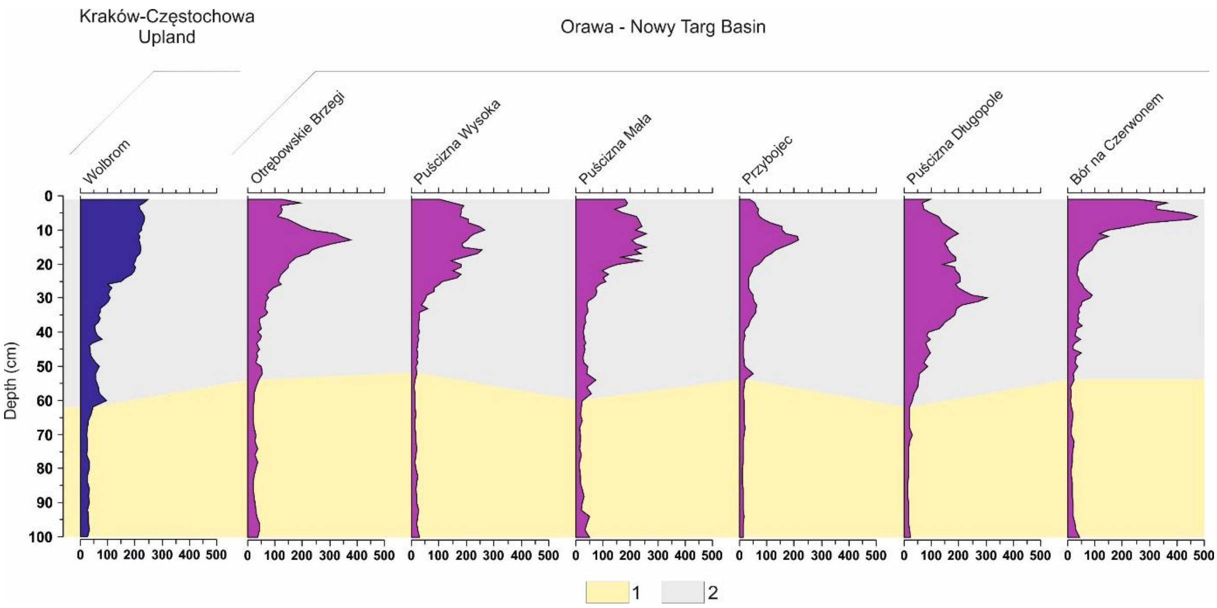

Fig. 5. Mercury concentration in the research raised bogs in the Małopolska region
1 – geochemical background of mercury content, 2 – anthropogenic enrichment

Table 2

Statistical indicators of natural (geochemical background) and anthropogenic concentrations of Hg (μg/kg) in the analysed peatlands of Małopolska region

Peat layers	Statistical results	Wolbrom	Otrębowskie Brzegi	Puścizna Wysoka	Puścizna Mała	Przybojec	Puścizna Długopole	Bór na Czerwonem
A layer of polluted sediments	Average	**124.8**	**119.6**	**111.4**	**111.3**	**65.0**	**129.6**	**103.9**
	Median	**100.3**	**100.0**	**100.7**	**75.7**	**50.3**	**140.0**	**49.1**
	Standard deviation	**78.2**	**88.5**	**83.5**	**82.5**	**53.8**	**69.3**	**120.9**
	Maksimum	**247.4**	**375.9**	**265.0**	**259.3**	**216.8**	**303.9**	**473.0**
	Minimum	**32.6**	**29.4**	**17.3**	**24.9**	**12.8**	**21.4**	**19.6**
Depth: 70–100 cm (geochemical background)	Average	29.0	30.1	20.0	25.0	12.6	16.6	20.8
	Median	28.3	28.5	19.3	21.2	12,4	16.4	18.6
	Standard deviation	3.3	7.6	4.5	12.5	1.6	2.9	7.3
	Maksimum	34.6	43.6	30.9	49.8	15.4	23.7	42.9
	Minimum	25.7	19.7	14.5	12.7	9.9	11.8	13.6

(Fig. 7). Here, mercury correlates strongly with mineral matter only (r=0.74), and slightly less so with lead (r=0.69) and potassium (r=0.68).

The Przybojec peat bog recorded the lowest concentration not only of mercury but also of copper and zinc (Fig. 6). In the vertical profile of peat sediments, lead peaks lowest down (at a depth of 15–16 cm), whereas, slightly higher up (12–13 cm), the contents of mercury, potassium and mineral matter reach their maxima. The highest share of copper occurs at a depth of 8–9 cm, while the maximum share of zinc is in the surface layer (0–1 cm). Compared to the Otrębowskie Brzegi site, there are far stronger correlations between mercury and several other geochemical variables (Fig. 7), namely mineral matter (r=0.84), lead (r=0.72), copper (r=0.71) and potassium (r=0.70), and slightly weaker correlations with zinc (r=0.64) and iron (r=0.60).

In the peat profile from the Bór na Czerwonem site, Cu, Zn and Pb contents peak in the topmost sample, at a depth of 0–1 cm. However, the highest concentrations of Hg and mineral matter and potassium appear slightly lower, at a depth of 4–5 cm (Fig. 6). In the sediments of this bog, the system of correlations between analysed geochemical variables was strongest (Fig. 7). Mercury is correlated most strongly with lead (r=0.81), iron (r=0.76), zinc (r=0.74) and potassium (r=0.70) and slightly less strongly with mineral matter (r=0.58) and copper (r=0.50).

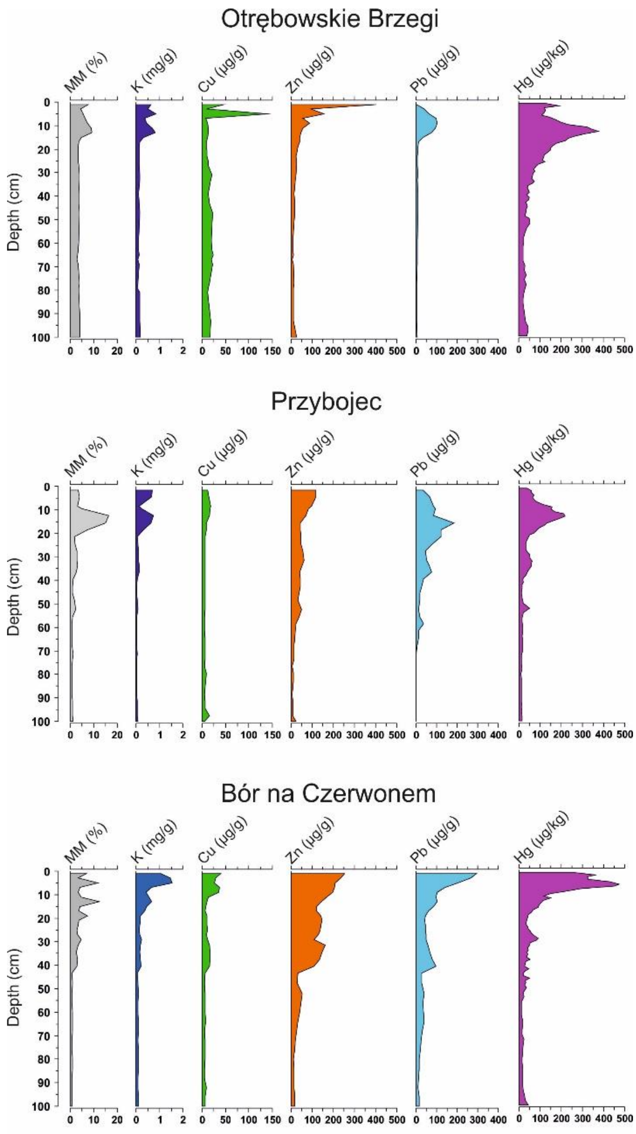

Fig. 6. The content of mineral matter (MM) and selected metals in research raised bogs of the Orawa-Nowy Targ Basin

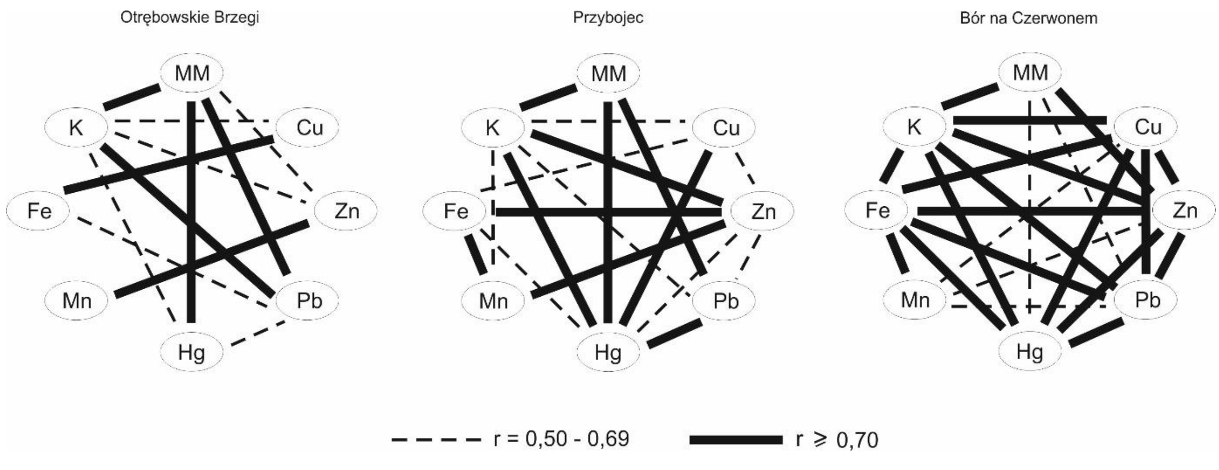

Fig. 7. Correlations between selected geochemical results in the surface layers of peat sediments (0–100 cm) from the raised bogs at Otrębowskie Brzegi, Przybojec and Bór na Czerwonem

Discussion

The mercury content in samples from raised bogs dating to the Early Holocene varies greatly across Europe (Fig. 8). In the surface peat layers at 50–0 cm, the concentration of this element usually increases quickly towards the surface. Usually, by a depth of ~50 cm, the Hg content is of the order of several to more than ten µg/kg, which can be considered the natural geochemical background. By contrast, near-surface mercury contents range from several hundred to over 1 000 µg/kg and are associated with human impact. The highest concentrations of Hg in Europe have been found in the Jeseniky peatlands in the Sudetes (Coufalík *et al.* 2013), at Misten Peat in the Eifel Mountains (Allan *et al.* 2013) and at Novodomské in the Kruszcowe Mountains (Zuna *et al.* 2012). Quite high Hg contents in excess of 500 µg/kg have also been found in peat bogs in Scotland (Farmer *et al.* 2009) and at the Bílá Smědá site in the Jizera Mountains. In many cases, isotopic methods (^{210}Pb, AMS ^{14}C and ^{241}Am) have been used to date samples with peak mercury contents (tab. 3).

Table 3

Accumulation time of peat samples containing peak Hg contents in selected European raised bogs

Area	Name of core	Maksimum concentration of Hg [µg/kg]	Age	References
Southern Norway	A – Gjerstad	204	65 BP	Steinnes i Sjøbakk (2005); Miszczak *et al.* 2020
	B – Gyland	349	34 BP	
Western Norway	C – Fure	196	180 BP	
Middle Norway	D – Namsos	106	20 BP	
	E – Nordli	146	65 BP	
Norway – Lofoty Islands	F – Andøya	364	27 BP	
Scotland – Turclossie Moss	TM04M-1	515	1967-1973 AD	Farmer *et al.* (2009)
Scotland – Flanders Moss	FM04-1-M	532	1943-1968 AD	
	FM01CM-2	625	1953-1967 AD	
Red Moss of Balerno	RM03CM-2	663	1926-1945 AD	
Carsegowan Moss	CM04CM-1	613	1930-1944 AD	
Belgium – Eifel Mountains	Misten Peat M1	840	1937-1965 AD	Allan *et al.* (2013)
	Misten Peat M4	1130	1930-1969 AD	
Czech Republic – Rudawy Mountains	Novodomské ND 3	~500	1963 ± 3 AD	Zuna *et al.* (2012)
Czech Republic – Izerskie Mountains	Bílá Smědá BS 2	~520	1980 ± 2 AD	
Czech Republic – – Szumawa Mountains	Jezerní JS 1	~240	1947 ± 4	
Czech Republic – Brdy Mountains	Core 1	~450	1987 ± 3	Ettler *et al.* 2008
	Core 2	701	1959 ± 10	
	Core 3	404	1965 ± 5	
Switzerland – Jura Mountains	Etang de la Gruère EGR2G	~450	1919 AD	Ross-Barraclough *et al.* (2002)

As Table 3 shows, the Hg concentration maxima in European raised bogs usually fell in the period from the 1930s to the 1970s. The stratigraphic analysis of the variability in Hg concentrations in the peat bogs whose mercury peaks were not dated (Biester *et al.* 2006; Martinez-Cortizas *et al.* 2007; Zaccone *et al.* 2009; Rydberg *et al.* 2010; Coufalík *et al.* 2013; Küttner *et al.* 2014; Smeds 2020) showed shows the maxima usually to occur within a few centimetres to a little over ten centimetres below the peat bog's surface. A similar situation was also documented in the Orawa-Nowy Targ Valley (Fig. 5). This shows a significant decrease in mercury pollution over recent decades. At the Otrębowskie Brzegi site,

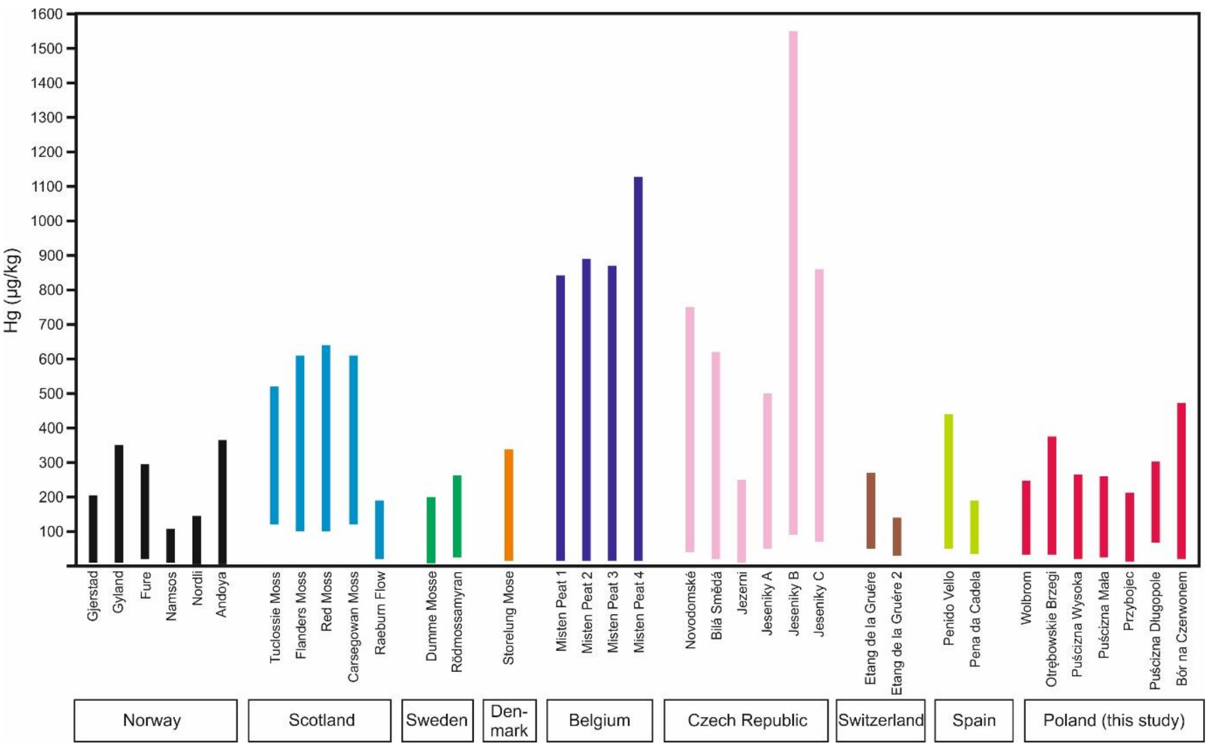

Fig. 8. The range of Hg concentration in selected European raised bogs in the layer up to 50 cm deep according to many authors: Norway (Steinnes, Sjøbakk 2005); Scotland (Farmer *et al.* 2009); Sweden (Biester *et al.* 2006; Rydberg *et al.* 2010); Denmark (Shotyk *et al.* 2003); Belgium (Allen *et al.* 2013); Czech Republic (Zuna *et al.* 2012; Coufalík *et al.* 2013); Switzerland (Ross-Barraclough *et al.* 2002; Zaccone *et al.* 2009); Spain (Martinez--Cortizas 1999; Biester *et al.* 2006); Poland (this study)

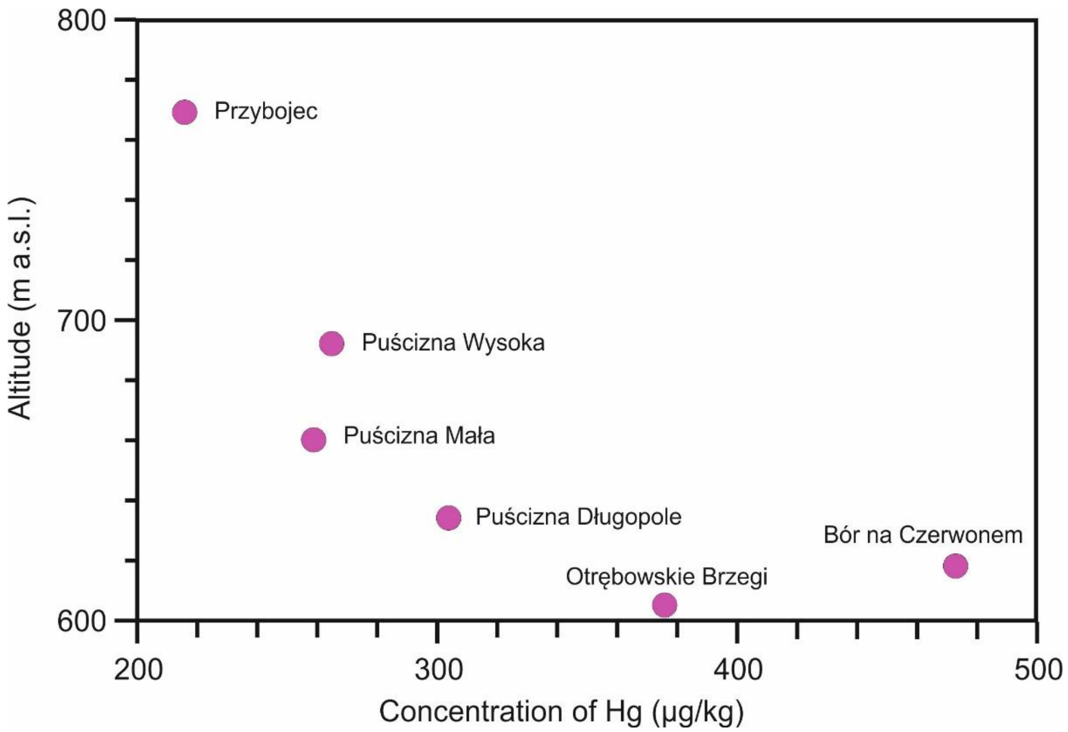

Fig. 9. The relationship between the Hg concentration and the altitude of the surface research raised bogs at the Orawa-Nowy Targ Basin

contamination with heavy metals, especially Cu and Zn, has also decreased in recent decades (Fig. 7). The works of Pawełczyk *et al.* (2018; 2019) have documented that contamination with Cu and Zn peaked in 1975±10 years. By contrast, at the Bór na Czerwonem site (Fig. 7), the high content of heavy metals increases up to the surface peat layer (0–1 cm).

Despite the proximity of Upper Silesia and its history of heavy industry, in the upper 25-cm layer of peat at the Wolbrom site, the mercury concentration was not very high but gradually increased (in the range of 150–250 μg/kg). This is probably because the east-west-oriented Wolbrom Gate is well ventilated by the prevailing westerly winds. Accordingly, the heavy metal contents here are not too high (Pawełczyk *et al.* 2017), and for Ni, Cr and Cu generally do not exceed natural background values (Pawełczyk *et al.* 2018). In this peat bog, in contrast to the others in Małopolska and other areas of Europe, mercury reaches its peak concentrations in the 0–1-cm surface layer. However, taking into account the aforementioned history of this peatland – its anthropogenic degradation initiated by drainage and consequent drying and moorshing of the uppermost peat layer – the currently observed variability in Hg content does not reflect the actual history of environmental pollution with this metal.

In the Orawa-Nowy Targ Basin, it was also found that the Hg concentrations are highest in the lowest peat bogs and decrease markedly with altitude above sea level (Fig. 9). This is probably related to the topoclimatic conditions prevailing in this area – and especially to the greater frequency of cold air stagnation and thermal inversions (which favour the persistence of smog and thus the precipitation of its heavy metal contents) at topographically lower locations. The lowest concentrations of mercury and other heavy metals (Cu, Zn, Pb) at the Przybojec site are probably due not only to it being the highest bog (tab. 1), but also to it occupying a well-ventilated watershed location. By contrast, the highest concentrations of analysed metals occur in the two lowest-lying peat bogs (Otrębowskie Brzegi and Bór na Czerwonem), which developed on low riverside terraces of the Czarna Orawa and Dunajec rivers. At the Bór na Czerwonem site, the immediate vicinity of Nowy Targ and its industrial zone is also significant.

The presented research results showed that, in all peat samples of the study area, the concentration of mercury did not exceed regional geochemical background values. According to the criteria for evaluating the quality of water sediments proposed by Bojakowska and Sokołowska (1998), it follows that all research samples fall into the first class of pollution. Concentrations of mercury were found to exceed the background level several-fold in the soils and water sediments other sites of this region (Pasieczna 2012, 2014; Baran *et al.* 2015). The reason for this is the mercury from low atmospheric emissions being supplemented by mercury from other sources, especially input wastewater discharged from factories producing chlorine and synthetic fibres, pulp mills and municipal wastewater discharge.

It should also be emphasised that increased mercury content in Holocene peatlands is not related to anthropogenic pressure alone, but also to the degree of peat decomposition, volcanic events and, indirectly, climate change (Martinez-Cortizas *et al.* 1999, 2007; Biester *et al.* 2002, 2006; Ross-Barracloud *et al.* 2002; Farmer *et al.* 2009; Zaccone *et al.* 2009; Allan *et al.* 2013; Küttner *et al.* 2014; Talbot *et al.*, 2017). Recent studies of the mercury cycle in Arctic and Antarctic regions (Bargagli 2016; Obrist *et al.* 2017; Olson *et al.* 2018, 2019; Jiskra *et al.* 2019; Pérez-Rodríguez *et al.* 2019) clearly indicate increased concentrations of this element in plants, soils and organic sediments of tundra areas. Research by Olson *et al.* (2019) also shows that the increased absorption of elemental mercury (H^0) by tundra vegetation is an important mechanism for increasing the deposition of this element in the environment. This happens through leaf fall and the death of peat-forming plants, especially non-vascular plants, which absorb the most mercury (Olson 2019). A clear impact of climatic conditions on mercury deposition in European peatlands is also documented by studies on the Eemian–Vistulian lake-marsh sediments (Mirosław-Grabowska *et al.* 2022).

Conclusions

After analysing the mercury content in 525 peat samples from seven 100-cm profiles collected from raised bogs in the Małopolska region (Wolbrom from the Kraków-Częstochowa Upland and Otrębowskie Brzegi, Puścizna Wysoka, Puścizna Mała, Przybojec, Puścizna Długopole and Bór na Czerwonem in the Orawa-Nowy Targ Basin), it was found that anthropogenic enrichment in this element usually covers a layer to a depth of 50–60 cm (Fig. 5). However, the maximum concentrations of Hg occur at various depths of usually a few to a little over ten centimetres below ground level. The course of the curves showing the variability of Hg content in the Małopolska region (Fig. 5), as well as the dated profiles of raised bogs from various parts of Europe, lead us to conclude (see Table 3) that environmental pollution with mercury has clearly decreased in the last few decades. Among the analysed peat bogs of the Małopolska region, only the site in Wolbrom found the mercury content to be highest in the surface layer of 0–1 cm, which may be associated with engineered drainage and resultant drying of the fen and moorshing of its surface layer.

The concentration of mercury in the raised bogs of the Orawa-Nowy Targ Basin (Otrębowskie Brzegi, Przybojec and Bór na Czerwonem) correlates significantly with the content of mineral matter, potassium and lead – – and additionally with zinc, iron and copper at the Przybojec and Bór na Czerwonem sites (Fig. 7).

The range of mercury content in the peat layer down to 50 cm deep in the analysed peat bogs of the Małopolska region is, compared against other European sites, similar to that in peat bogs of Norway, Sweden, Denmark and Spain, and decidely lower than that in peat bogs of Scotland, Belgium and Czechia (Fig. 8).

In the peat bogs of the Orawa-Nowy Targ Basin, there was a clear increasing trend in mercury levels, the higher the altitude of the bog surface. This is probably related to the prevailing local topoclimatic conditions, and in particular to the greater frequency of cold air stagnation and thermal inversions, which favour the persistence of smog at the lowest altitude sites.

The research to date on mercury content in the sediments of raised bogs of the Małopolska region will be extended to new sites in the Orawa-Nowy Targ Basin, and further enriched with geochronological data (^{14}C and ^{210}Pb dating), geochemical and palynological data, which will help determine the history of mercury deposition in the changing post-glacial and Holocene climate conditions in the area.

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