Original Research Variations in the Chemical Composition of Bottom Deposits in Anthropogenic Lakes

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Abstract

South-central Poland has thousands of anthropogenic lakes. Our study investigated the diversity of the chemical composition and concentration of trace elements in the lake bottom deposits. Particle size distribution was determined using sieve analysis and the combined areometric-sieve method. Concentrations of oxides $(SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5)$ were determined in sediments using the ICP method. Moreover, loss on ignition was measured and concentrations of Zn, Pb, Cu, Cd, and Ni were determined. Concentrations of As, Ba, Cs, Cr, Co, Ag, and Th were determined using the INAA method. Study results revealed considerable variation in the particle size distribution and chemical composition of bottom sediments. In broad terms the dominant grain size is >0.1 mm. Two other fraction sizes account for roughly equal proportions of the rest, i.e. 0.1-0.02 mm and <0.02 mm. As concerns overall composition, SiO₂ dominated in samples, particularly those where loss on ignition was low. Bottom sediments in the lakes varies in chemistry and pollution levels. The scale of pollution is illustrated by the range of variability of average contents of trace elements in the bottom deposits, e.g.: As (7-63 mg·kg⁻¹), Ba (262-1,630 mg·kg⁻¹), Cs (1.6-134.0 mg·kg⁻¹), Zn (83-3,720 mg·kg⁻¹), Pb (28-731 mg·kg⁻¹), Cr (22-146 mg·kg⁻¹), Cd (0.5-50.3 mg·kg⁻¹), and Cu (9-197 mg·kg⁻¹). The deviations from geochemical background standards found in the bottom sediments of the water bodies examined make them exceptional on a global scale.

Keywords: water bodies, lake, bottom sediments, chemical composition, trace elements

Introduction

The contact zone between river and lake waters provides a convenient location for the accumulation of debris material in all water bodies. The energetic conditions of water flow change in this zone and deltas or alluvial fans and accumulations of bottom sediments form as a result of debris sedimentation. Organic matter sedentation processes, which are of particular morphogenetic importance in areas that periodically dry up, also play a significant role. The supply of material from the atmosphere also contributes to the silting of water bodies; this is especially significant for water bodies with no tributaries. Water body basins are places where the material forming bottom sediments accumulates and they thus serve as sedimentation basins to some extent; bottom sediments may record the geomorphological phenomena and processes that take place in that environment [1].

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South-central Poland (the Upper Silesian region) includes thousands of anthropogenic lakes [2]. The largest number have formed in subsidence basins, followed by abandoned exploitation pits, river dam projects and dyke-retained ponds that combined create the largest complex of water bodies in southern Poland. The water bodies examined have mostly formed in recent decades and are relatively new subjects for bottom sediment studies. Their scientific importance is enhanced by the fact that the area where they are present is considered the most anthropogenically transformed part of Poland. No large-scale bottom sediment studies in the Upper Silesia region [3-5]. They were carried out within not numerous water reservoirs used for recreation or water supply for different purposes [6, 7].

The study investigated the diversity of the chemical compositions and concentrations of trace elements in the lake bottom deposits. The analysis of the chemical composition of bottom sediments is of key importance for initiating further studies concerning their environmental importance and the possibility of exploiting them for commercial purposes.

Experimental Procedures

Bottom sediments were studied in 20 anthropogenic water bodies in the central part of southern Poland (Fig. 1). This area is considered the most anthropogenically transformed part of Poland. The water bodies selected for the study had varied origins, dimensions, and hydrochemistry. These are anthropogenic water bodies (reservoirs impounded by dams, flooded mineral workings, levee ponds, water bodies in subsidence basins) that represent the types of water bodies commonly found in Upper Silesia (i.e. in the central part of southern Poland). The water bodies selected for the study are subject to different degrees of anthropogenic pressure, which makes them unique study sites in comparison to lakes that are ecosystems without strong anthropogenic impact.

Bottom sediment samples were collected from the water reservoirs in 2007 and 2008 using a sediment core sampler operated from an ice cover. The sampler was submerged on a steel line using a hand-operated winch. Bottom deposit samples were collected both in the zone along the reservoir axis and within bays and in maximum depth locations.



Fig. 1. Study area location with anthropogenic water bodies marked:

1 – Pławniowice, 2 – Dzierżno Małe, 3 – Dzierżno Duże, 4 – Osadnik Kłodnicy, 5 – Makoszowy – subsidence zone, 6 – Żabie doły – SE basin, 7 – Żabie doły – NE basin, 8 – Kozłowa Góra, 9 – Przeczyce, 10 – Pond at the mouth of the Mitręga, 11 – Pogoria I, 12 – Pogoria II, 13 – Pogoria III, 14 – Pekin – N basin, 15 – Bobrek ¬(floodplain), 16 – Sławków pond, 17 – Water body in Jaworzno, 18 – Harmęże pond, 19 – Żory pond, 20 – Lubomia pond.

Legend: 1 - surface waters, 2 - state border, 3 - main cities.

No samples were collected in the littoral zone, where the chemical composition of sediments often corresponds to the geochemical properties of the material found on the shore [8, 9].

Sediment samples were collected using polyethylene and polystyrene containers and a polystyrene sediment core sampler. The material collected was dried at 105°C. Particle size distribution was determined using sieve analysis and the combined areometric-sieve method. After they had been dried, the samples were homogenized using an agate mill. The samples prepared in this manner were then subjected to laboratory analyses in ACTLABS (Activation Laboratories Ltd.) in Canada.

Concentrations of certain oxides (SiO₂, TiO₂, Al₂O₃, Fe2O3, MnO, MgO, CaO, Na2O, K2O, P2O5, loss on ignition) and elements (Zn, Pb, Cu, Cd, and Ni) were determined in sediments using the ICP method (total digestion inductively coupled plasma). A 0.25 g sample aliquot is digested with HClO₄-HNO₃-HCl-HF at 200°C to fuming and is then diluted with aqua regia. This leach is partial for magnetite, chromite, barite, and other spinels and potentially massive sulphides. Concentrations of As, Ba, Cs, Cr, Co, Ag, and Th were determined using the INAA method (instrumental neutron activation analysis). A 1 g aliquot is encapsulated in a polyethylene vial and irradiated with flux wires and an internal standard (1 for 11 samples) at a thermal neutron flux of 7×10^{12} n cm⁻²·s⁻¹. After a 7-day decay to allow Na-24 to decay, the samples are counted on a highpurity Ge detector with resolution of better than 1.7 KeV for the 1332 KeV Co-60 photopeak.

Quantification levels for loss on ignition and for most oxides were 0.01% with the exception of TiO_2 , for which the level was 0.005%. The detection limit of 0.5 mg/kg concerned Ag, Cd, Cs, and Th. For Cu, Co, Ni, and Zn, the detection limit was 1 mg/kg. For As and Cr, the detection limit was 2 mg/kg, while for Ba it was 3 mg/kg, and for Pb – 5 mg/kg.

Results

Study results revealed considerable variation in the particle size distribution and chemical composition of bottom sediments.

The granularity of the deposits depended primarily on catchment lithology and the type of rubble supplied. Anthropogenically stimulated rubble supply (resulting from altered discharge conditions, household waste water, municipal waste water, sewage sludge) and changing sedimentation conditions (fluctuating water table, vegetation overgrowing, bank processes) result in a lack of one clearly dominant granularity in the mechanical composition of the deposits, which vary greatly from lake to lake (Fig. 2). In broad terms the dominant grain size is >0.1 mm. Two other fraction sizes account for roughly equal proportions of the rest, i.e. 0.1-0.02 mm and <0.02 mm. Closer to the edges of water bodies, the sandy fraction usually dominates, while within the bottom proper argillaceous and dust particles prevail.

Bottom sediments in the lakes varies in chemistry and pollution levels (Tables 1 and 2). The scale of pollution is

illustrated by the range of variability of average contents of trace elements in the bottom deposits, e.g.: As (7-63 mg·kg⁻¹), Ba (262-1,630 mg·kg⁻¹), Cs (1.6-134.0 mg·kg⁻¹), Zn (83-3,720 mg·kg⁻¹), Pb (28-731 mg·kg⁻¹), Cr (22-146 mg·kg⁻¹), Cd (0.5-50.3 mg·kg⁻¹), and Cu (9-197 mg·kg⁻¹).

In this respect the analysis concludes that the main problem was the exceedance of the background geochemical level. Owing to the complex geological structure, in which pre-Quaternary rocks of different types and mineral compositions (e.g. Middle Triassic dolomites and limestones, Carboniferous sandstones with carbon inserts) lie adjacent to one another on the surface, and the considerable diversity of surface Quaternary deposits that have been subject to several centuries of anthropogenic pressure, any comparisons of study results to the geochemical background in Upper Silesia are difficult, even within a single catchment, and caution is required in the interpretation of results. Therefore results for bottom sediments have been deliberately compared to the levels considered natural, which have been defined very broadly, i.e. for all types of sedimentary rocks. This way of presenting data appears the most advantageous not only from the point of view of showing differences in the chemical composition of sediments, but also with respect to demonstrating the magnitude of anthropogenic impact.

Discussion

Bottom deposits in water bodies in the Upper Silesia region are irregular accumulations of mineral or organic





1 – Pławniowice, 2 – Dzierżno Małe, 3 – Dzierżno Duże, 4 – Osadnik Kłodnicy, 5 – Makoszowy – subsidence zone, 6 – Żabie doły – SE basin, 7 – Żabie doły – NE basin, 8 – Kozłowa Góra, 9 – Przeczyce, 10 – Pond at the mouth of the Mitręga, 11 – Pogoria I, 12 – Pogoria II, 13 – Pogoria III, 14 – Pekin – misa N, 15 – Bobrek (floodplain), 16 – Sławków Pond, 17 – Water body in Jaworzno, 18 – Harmęże Pond, 19 – Żory Pond, 20 – Lubomia Pond.

Water body name or location	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Loss on ignition
	[%]										
Pławniowice	45.05	6.96	2.26	0.05	0.55	13.43	0.40	1.22	0.52	0.33	27.21
Dzierżno Małe	39.09	7.45	3.24	0.07	0.80	19.47	0.40	1.27	0.45	0.29	25.88
Dzierżno Duże	28.60	10.78	5.37	0.06	1.53	1.96	0.43	1.46	0.46	1.00	45.74
Osadnik Kłodnicy	20.80	7.14	4.26	0.05	1.49	2.53	0.20	1.04	0.28	0.46	58.89
Makoszowy – subsidence zone	79.94	6.53	2.60	0.03	0.38	0.66	0.67	1.61	1.02	0.07	7.06
Żabie doły – SE basin	59.79	7.93	4.85	0.14	0.68	6.58	0.63	1.69	0.62	0.24	16.26
Żabie doły – NE basin	71.67	7.76	6.37	0.26	0.54	1.67	0.68	1.93	0.65	0.13	7.68
Kozłowa Góra	55.74	8.23	4.79	0.09	0.50	1.88	0.47	1.27	0.54	0.30	25.67
Przeczyce	45.38	8.18	6.53	0.16	0.91	8.06	0.35	1.39	0.53	0.52	26.84
Pond at the mouth of the Mitręga	50.88	8.63	4.58	0.08	1.88	9.51	0.40	1.50	0.57	0.20	20.52
Pogoria I	64.00	12.13	9.37	0.17	1.14	2.13	0.55	2.21	0.79	0.22	6.85
Pogoria II	64.50	11.80	9.30	0.16	1.14	2.13	0.55	2.28	0.81	0.15	7.18
Pogoria III	65.22	11.84	4.17	0.08	1.74	3.47	0.60	2.28	0.81	0.10	9.33
Pekin – N basin	46.66	11.91	9.55	0.19	0.71	3.85	0.35	1.67	0.65	0.23	23.59
Bobrek (floodplain)	21.05	6.60	11.71	0.46	1.32	6.18	0.29	0.96	0.35	5.28	42.52
Sławków Pond	21.64	3.71	3.00	0.07	6.08	26.74	0.21	0.62	0.22	0.08	33.91
Water body in Jaworzno	6.48	1.16	4.68	0.39	13.70	30.60	0.05	0.15	0.06	0.06	42.11
Harmęże Pond	65.31	12.70	5.49	0.05	1.11	0.49	0.89	2.02	0.82	0.26	9.71
Żory Pond	67.07	6.49	2.64	0.04	0.39	1.17	0.68	1.50	0.65	0.22	18.27
Lubomia Pond	74.43	9.55	3.05	0.03	0.75	0.82	0.93	2.11	0.72	0.19	7.83

Table 1. Average basic chemical composition of bottom sediments in select water bodies in central southern Poland.

material (and less often sediment covers) whose formation rates depend on the abundance of supply of various types of debris. Atmospheric supply is usually considered a much less important factor in the formation of bottom sediments; nevertheless, as demonstrated by earlier studies [4], its role increases significantly for water bodies with no tributaries - on the condition, however, that dry and wet deposition material is aggregated in the water and subject to gravitational transport (i.e. sediments are lifted and moved). The rate of debris supply to water bodies under significant anthropogenic pressure is comparable to the rate at which mineral matter is supplied to reservoirs impounded by dams in areas where erosive features clearly are present. The results of research on shallowing of lakes carried out by Ławniczak et al. [10] indicate that the rate of reservoir silting can be faster. Therefore the rate at which these water bodies become shallower is much faster than for lakes, and the mechanical composition of sediments deposited in water body basins shows very wide variation.

The particle size distribution of bottom sediments depends primarily on the original substrate of the water

body basin and on the type of debris supplied from the catchment area. Due to the age of sediments (which frequently does not exceed several decades) and sometimes due to their movement and mixing, no single fraction clearly dominates in their mechanical composition and sediments exhibit many peculiar features that are difficult to interpret (Fig. 2); moreover, individual water bodies tend to be very different. This is caused by the following factors: natural processes forming the bottom of the water body when filled with water, water mixing processes, varying effectiveness of morphogenetic processes in dry areas when water levels are low, water organism activity, and human mechanical intervention.

The scale of the anthropogenic impact in determining the basic chemical composition of bottom sediments (Table 1) and the trace element content (Table 2) of the water bodies under examination can be illustrated by making comparisons with geochemical background levels defined for sedimentary rocks [11], and similar data from selected lakes in Poland [12-14] and various regions of the world [15, 16].

Water body name or loca-	As	Ba	Cs	Cr	Zn	Cd	Со	Cu	Ni	Pb	Ag	Th
tion	[mg·kg ⁻¹]											
Pławniowice	13.1	460.0	3.6	66.0	407.9	17.7	11.1	23.6	19.0	89.6	0.8	13.1
Dzierżno Małe	12.3	449.1	4.5	66.1	342.6	2.4	14.8	21.5	23.8	69.6	0.8	12.3
Dzierżno Duże	23.0	1333.7	9.8	119.3	801.7	9.8	22.3	93.7	30.3	133.7	2.1	23.0
Osadnik Kłodnicy	15.0	1630.0	6.5	58.0	300.0	1.6	18.0	72.0	46.0	70.0	< 0.5	15.0
Makoszowy – subsidence zone	7.0	379.0	2.6	100.0	417.0	5.5	6.0	9.0	14.0	32.0	0.9	7.0
Żabie doły – SE basin	53.0	725.0	5.8	72.0	2480.0	22.3	15.0	62.0	34.0	708.0	1.0	53.0
Żabie doły – NE basin	60.0	543.0	4.6	62.0	3560.0	20.6	13.0	19.0	32.0	542.0	1.0	60.0
Kozłowa Góra	41.0	1080.0	5.1	74.0	1729.0	18.1	16.0	60.0	26.5	479.0	0.6	41.0
Przeczyce	31.0	524.5	7.6	82.5	1443.0	13.0	15.0	36.0	28.0	533.0	0.9	31.0
Pond at the mouth of the Mitręga	15.0	431.0	6.6	70.0	961.0	9.2	13.0	27.0	25.0	731.0	0.8	15.0
Pogoria I	24.5	736.5	8.6	136.0	1798.0	22.3	22.0	53.0	48.0	336.0	1.3	24.5
Pogoria II	12.8	524.5	8.3	111.0	288.0	2.4	18.1	34.0	33.0	69.6	1.0	12.8
Pogoria III	10.4	428.8	8.3	103.9	181.3	0.9	15.5	19.4	32.9	49.8	1.0	10.4
Pekin – N basin	37.0	863.0	8.6	77.0	1240.0	9.7	35.0	50.0	41.0	332.0	0.6	37.0
Bobrek (floodplain)	22.0	1380.0	134.0	146.0	3720.0	50.3	36.0	197.0	85.0	568.0	67.0	22.0
Sławków pond	34.0	393.0	4.0	53.0	2910.0	10.5	4.0	21.0	17.0	473.0	0.7	34.0
Water body in Jaworzno	63.0	262.0	1.6	22.0	1090.0	5.5	3.0	16.0	12.0	162.0	0.6	63.0
Harmęże pond	10.0	460.0	7.2	123.0	177.0	1.2	16.0	28.0	50.0	52.0	< 0.5	10.0
Żory pond	17.0	386.0	3.0	69.0	138.0	1.8	7.0	22.0	19.0	65.0	< 0.5	17.0
Lubomia pond	12.0	453.0	5.0	70.0	83.0	0.5	7.0	21.0	25.0	28.0	< 0.5	12.0

Table 2. Concentrations of select trace elements in bottom sediments in water bodies in central southern Poland.

As concerns overall composition, SiO_2 dominated in samples, particularly those where loss on ignition was low (Table 1). Variations in the chemical composition of sediments between individual water bodies are determined by type of debris, the manner in which the catchment is utilized, and the geological substrate. A high loss on ignition indicates significant organic matter content. This matter is usually allochthonous. Additionally, zones near lake edges often are colonized by compact rush and willow stands that exhibit high bioproductivity. The plant fall originating there has as significant an impact on the chemical composition of sediments as autochthonous matter.

Where trace element concentrations in bottom sediments are higher than those usually found in sedimentary rocks [11], this is a primary indicator of anthropogenic pressure [17]. This is particularly visible with respect to elements such as Zn, Cd, or Pb; for cadmium, the concentration found in the bottom sediments of some water bodies was two orders of magnitude higher than natural concentration levels (0.05-0.35 mg·kg⁻¹); at some locations, the ratio exceeded one hundred. As concerns lead content (natural concentrations for this metal are usually considered to range from a few [15] to 40 mg·kg⁻¹ [11]), the lower limit of the background defined in this manner was exceeded several hundred times, and the upper limit was only exceeded between ten and twenty times. Only some elements, e.g. Cs, Co, Ni, Ag, or Th, were present in bottom sediments at normal background or similar levels (Table 2).

The lowest trace element concentrations – often similar to the levels considered natural – were found in water bodies in quasi-natural areas, and those that were effectively isolated from the supply of various pollutants. This criterion is met by the Dziećkowice water body, which is fed by the Carpathian tributaries of the Vistula River [18] and its water and sediments exhibit zero or very low pollution levels [19]; therefore it is used to supply water for human consumption. Somewhat higher trace element concentrations were found in areas where urban and agricultural anthropogenic pressure was present. In most cases, the causes of high concentrations of those elements can be explained by the supply of pollutants from urban and industrial areas. The highest pollution levels are regularly exhibited by sediments in water bodies that are situated close to ore-bearing formations and in the vicinity of slag heaps and steelworks.

Bottom sediments in most water bodies are contaminated with heavy metals. Concentrations of these elements are higher than those found in preindustrial alluvia in the Przemsza River [20] and in alluvial deposits in the upper reaches of the Vistula River [21]. High heavy metal concentrations in sediments are particularly dangerous to the environment in connection with the increasing trend toward acidification of the environment that has been observed for many years [22-26], while the alkalizing effect of atmospheric dust is being minimized [27, 28]. Toxicity of heavy metals mobile forms for ecosystems, especially in the situation of acidification, is emphasized by Wojtkowska [29], who has been investigating the deposits of Lake Czerniakowskie. Therefore the potential increase in the acidity of limnic water in some water bodies is a real threat associated with the unhindered increase in the mobility of the metals currently accumulated in bottom sediments [30] and their movement to other areas linked by hydrographic drainage axes. The pollution of certain water body ecosystems with heavy metals already poses a hazard to human health; the concentrations recorded in phyto- and zooplankton, vascular plants, and ichthyofauna point to serious contamination [31].

The presence of pollutants in the bottom sediments of the water bodies studied also has been confirmed by the comparison of study results with the geochemical background determined for surface water sediments in the Silesia and Kraków regions [13]. Geochemical background for As (6 mg/kg), Ba (98 mg/kg), Cu (15 mg/kg), Ni (11 mg/kg), Cr (9 mg/kg), Co (4 mg/kg), Pb (59 mg/kg), and Zn (259 mg/kg) is exceeded in almost every case – in some cases the levels are many times higher. As concerns the concentration of Cd, the situation is not clear-cut; geochemical background in the region is 2.5 mg/kg, which indicates the presence of pollution in some water bodies. With respect to one water body, even silver is present at levels much higher (69 mg/kg) than natural ones (1 mg/kg).

Comparisons of study results with geochemical background for Poland [12], where natural levels of the elements in question are lower (As < 5 mg/kg, Ba < 51 mg/kg, Cu - 6 mg/kg, Ni - 5 mg/kg, Cr - 5 mg/kg, Co - 2 mg/kg, Pb - 10 mg/kg, Zn - 48 mg/kg, Cd < 0.5 mg/kg, Ag - 0.5 mg/kg) yield similar results, i.e. indicate that bottom sediments of the water bodies studied are indeed polluted.

The deviations from geochemical background standards found in the bottom sediments of the water bodies examined make them exceptional on a global scale. This is revealed by comparative studies of heavy metal content in bottom sediments of many water bodies around the world. Only a few water bodies in the world exhibit higher concentrations of Cr - e.g. sediments of Taihu Lake in China [32], Ni – e.g. sediments of lakes in the vicinity of Murmansk in Russia [33], those of Lake Nasser reservoir in Egypt [34] and Lake Hazar in Turkey [35], Cd – e.g. sediments of the Pulicat Lake in India [36], or Cu – e.g. sediments of the aforementioned lakes in the vicinity of Murmansk in Russia [33], lakes in Stockholm [37], and Kolleru Lake in India [38]. As concerns Zn and Pb concentrations in bottom sediments, no water bodies can be found worldwide that could be compared to those in Upper Silesia [18].

Conclusions

Bottom sediments in lakes varies in chemistry and pollution levels. In this respect the analysis concludes that the main problem was the exceedance of the background geochemical level. The deviations from geochemical background standards found in the bottom sediments of the water bodies examined make them exceptional on a global scale.

The studies carried out demonstrate that the bottom sediments of water bodies are a good indicator of the environmental characteristics of the surrounding area. By documenting the role of natural and anthropogenic factors in determining their quantity, particle size distribution, chemical composition, and physical and chemical properties, they are an excellent record of the phenomena and processes that take place in the geographical environment of the catchment and around the water body itself. This also underlines their role as an excellent indicator of environmental change and as a factor related to the dynamic evolution of anthropogenic lakes as ecosystems.

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