Heavy metals risk assessment in water and bottom sediments of ICOLLs in northern Poland

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Abstract Natural diversity of intermittently closed and open lakes and lagoons (ICOLLs) depends on mutual interactions of several factors: (i) an impact of sea water and land background; (ii)temporary meteorological situation; (iii) hydrological conditions; and (iv) the shape of lake basin. However, some regional, local or even sudden impacts including anthropogenic ones create their final ecological status. To identify heavy metals risk assessment in ICOLLs located in Polish coastline selected metals were determined in water and bottom sediment samples collected in 10 water reservoirs. Multidimensional data set of 22 variables was explored by the use of chemometrics according to seasonality (Spring, Summer, Autumn), sample type (water, sediment) and level of isolation (fully isolated, partially and fully connected lakes). The results showed that 70% and 77% of the data variance can be explained by the use of principal component analysis for waters and sediments, respectively. Waters of fully isolated or partially connected lakes are more abundant with Ho, Ir, Nd and Sm, while less abundant with Pr and Sr. Some ICOLLs are spatially diversified according to Al, Fe, Mn, Ti, V and Yb indicating an anthropogenic impact due to periodical backwash of absorption filters in municipal water treatment plants located nearby.

Keywords: Baltic Sea, coastal lakes and lagoons, heavy metals, multivariate analysis, spatiotemporal variation

1. Introduction

One of the most emerging issues related with anthropopressure concerns contamination of aquatic ecosystems' compartments by heavy metals. Major heavy metals of environmental concern include As, Cd, Cr, Cu, Ni, Ag, V, Zn, Pb and Hg, however other metals are also important. Metals enter water reservoirs in both, dissolved and particulate phase from variety of sources (i.e. domestic, industrial, agriculture runoff, atmospheric deposition). The relatively high solubility of metals results in their uptake, and hence bioaccumulation, in aquatic plants and organisms. Heavy metals in particulate phase can be deposited as bottom sediments which could be also considered as a secondary source of metals due to remobilization resulting in their gradual release to the water reservoir or to aquatic organisms.

Despite the fact that a range of studies have been conducted on the most popular heavy metals distribution in water and bottom sediments (Elkady *et al*., 2015) only several describe coastal water bodies (Hernández-Crespo and Martín, 2015; Ivanter *et al*., 2016), a few describe individual coastal lake of Polish coast (Daniszewski and Konieczny, 2013) while none of them describe series of Polish ICOLLs and such huge range of metals as reported in this study. Therefore, the aim of the study was to assess variation of concentration of 22 metals in 10 ICOLLs according to seasonality and level of their relation to the Baltic Sea by the use of chemometrics.

2. Materials and methods

2.1. Study sites

Water and bottom sediment samples were collected in 2014 from 10 coastal lakes located in northern Poland: Ptasi Raj, Łebsko, Jamno, Gardno, Dołgie, Kopań, Wicko, Sarbsko, Resko and Liwia Łuża. Their detailed GPS location as well as hydrochemical properties including the name of the feeding stream, hydrological connectivity and Venice and hydrographic classifications are presented elsewhere (Obolewski *et al*., 2015). The information significant for this study is that coastal lakes represent three levels of isolation, i.e.: fully isolated (I), partially (PC) and fully connected (FC) with the Baltic Sea.

2.2. Sampling and analytical technique

Water and sediment samples (4-11) were collected from the boat in locations established according to the longest vertical and horizontal transects conducted across the lake.

Sampling was performed according to the procedure presented by Astel *et al*. (2016) and Ivanter *et al*. (2016) for water and bottom sediments, respectively. Analytical measurements were performed 3 times a year, starting in April and finishing in November to cover Spring, Summer and Autumn seasons. The inductively coupled plasma optical emission spectrometer Agilent 5100 ICP-OES (Agilent, USA) has been used in multielemental determination (Al, B, Ba, Bi, Cr, Cu, Fe, Ho, In, Ir, Mn, Nd, Ni, Pb, Pr, Sm, Sr, Ti, Tl, V, Yb and Zn). The synchronous vertical dual view (SVDV) of the plasma has been accomplished by using dichroic spectral combiner (DSC) technology which allows the axial and radial view analysis simultaneously. The common conditions have been used: Radio Frequency (RF) power 1.2 kW, nebulizer gas flow 0.7 L min-1, auxiliary gas flow 1.0 L min-1, plasma gas flow 12.0 L min-1, Charge Coupled Device (CCD) temperature -40°C, viewing height for radial plasma observation 8 mm, accusation time 5 s, 3 replicates. All reagents used are of analytical purity. Deionized ultrapure water produced in a Milli-Q device (Millipore, Saint Luis, USA) has been used. For sample and reference materials preparation the 65% nitric acid (Merck, Darmstadt, Germany) has been used. For ICP-OES analysis the ICP commercial analytical standards (Romil, England) have been used. The detection limits have been determined as 3-sigma criteria and were on the level of 0.001 mg L^{-1} and 0.01 mg kg^{-1} dry weight (DW) for all elements determined. The uncertainty for complete analytical process (including sample preparation) was at the level of 20%. The standard reference materials CRM S-1 – loess soil; CRM NCSDC (73349) – bush branches and leaves; CRM 2709 – soil; CRM 405 - estuarine sediments; CRM 667- estuarine sediments have been used for analysis quality control. The recovery (80-120%) was acceptable for all the elements determined. Detailed information has been published in previous work (Siwulski *et al*., 2017).

3. Results and discussion

Metals concentration in water and sediment samples according to the level of lakes isolation as well as ratio between their concentration in both compartments are shown in Table 1. Except for Mn, the concentration of Pb, Cu, Cr and Ni is little higher than reported by Elkady *et al*. (2015) for lake Manzala characterized by brackish water. Omitting seasonal and spatial variation mean concentration in water decreases in the following order: B>Zn>Fe>Al>Ho>Sr>Mn>Pb>Ni>Cr>Pr>Ba>Cu>Bi>Nd>V,Ti,Sm>In>Ir>Tl>Yb, while in bottom sediments in the following one:

Table 1. Mean concentrations of metals in water [mg L^{-1}]and bottom sediments [mg kg^{-1}] in ICOLLS of various connectivity with the Baltic Sea.

	coastal lake water (w)				bottom sediment (s)				
	Mean	Mean(FC)	Mean(PC)	Mean(I)	Mean	Mean(FC)	Mean(PC)	Mean(I)	Ratio s:w
Al	0.761	0.549	1.375	0.534	5143.443	4831.386	7096.646	4119.152	6763
B	1.379	1.220	1.403	1.473	138.198	172.703	140.178	114.873	100
Ba	0.029	0.035	0.026	0.026	50.650	20.636	120.897	25.837	1755
Bi	0.014	0.011	0.016	0.015	20.317	21.197	24.733	16.986	1413
Cr	0.037	0.035	0.039	0.038	26.491	16.006	55.525	12.972	713
Cu	0.019	0.019	0.021	0.018	54.654	44.003	101.557	32.078	2855
Fe	0.873	0.571	1.153	0.909	46949.505	53316.316	52866.690	39166.644	53791
Ho	0.643	0.557	0.699	0.669	25281.718	34923.094	26314.917	18463.766	39290
In	0.010	0.009	0.011	0.011	360.163	438.018	375.248	301.285	34739
Ir	0.003	0.002	0.004	0.004	14.199	15.996	14.500	12.861	4268
Mn	0.169	0.189	0.182	0.147	3387.995	5197.093	3816.401	1961.705	20074
Nd	0.012	0.006	0.016	0.014	592.710	778.411	648.068	439.170	48225
Ni	0.067	0.045	0.098	0.063	53.893	47.345	71.052	47.331	809
Pb	0.074	0.061	0.094	0.071	52.008	45.056	70.732	44.724	705
Pr	0.030	0.052	0.021	0.021	27.634	24.435	38.578	22.824	907
Sm	0.010	0.006	0.012	0.012	21.345	17.361	27.118	20.277	2118
Sr	0.572	1.280	0.163	0.285	27.809	39.630	34.155	15.036	49
Ti	0.010	0.006	0.017	0.007	168.244	149.421	200.171	157.791	17592
Tl	0.002	0.001	0.002	0.002	62.259	62.491	75.987	52.953	40326
V	0.010	0.008	0.012	0.009	33.985	29.096	42.796	32.224	3565
Yb	0.001	0.001	0.001	0.001	36.497	39.879	42.040	30.671	31807
Zn	1.003	0.791	1.241	1.004	2735.190	1860.564	5319.676	1619.032	2727

Ti>V>Al>Cu>B>Ba>Nd>Sr>Yb>Ho>Sm>Pr>Cr>Tl>Zn>Fe>Mn>Ni>In>Pb>Ir>Bi.

The results revealed that in case of several metals (Fe, Zn, Pb) relative high concentration in water corresponds with relative low concentration in sediments and vice versa, indicating that some metals were settled and accumulated in the sediments. Assuming water density as 1000 g L^{-1} the highest ratios between sedimental concentration and water concentration were found for Fe, Ho, In, Mn, Nd, Ti and Tl.

Six and four independent factors explaining 70% and 77% of the cumulated variance of the entire data set were distinguished for water and bottom sediment samples, respectively. For water samples their composition according to the metal influence and percentage of explained variance were as follows: F1: Ho, Ir, Nd, Sm, Pr(-), Sr(-) - 24%; F2: Al, Fe, Mn, Ti, V, Yb - 21%; F3: Cu, Zn - 6%; F4: B, Bi - 7%; F5: Pb, Tl - 6%; F6: Ba(-) - 6%. In case of sediment samples corresponding composition and percentage of explained variance were as follows: F1: Al, Ba, Bi, Cu, Ni, Pb, Ti, Zn - 24%; F2: Ho, In, Nd, Tl, Yb - 25%; F3: Be, Fe, Ir, Mn, Nd, Sm, V -18%; F4: Fe, Ir, Pr, Sr - 10%. Negative sign written next to the metal indicates indirectly proportional correlation with the rest of metals included to the particular factor. The relation between identified factors and ICOLLs types as well as seasonality was identified by the visualization of factor scores in various combination of factors. An existence of high values of factor scores and positive correlation coefficient between a given metal within a factor correspond to its high influence, and hence high concentration of the metal correlated with this factor in water or sediment sample. On the contrary, negative sign of a correlation coefficient joined with a high, positive value of a factor scores indicates low influence of a given component, and hence low concentration of metal contributing such factor. Plot of sample scores of F1 vs F2, F3 vs F4 and F5 vs F6 for waters visualized according to the lakes, including its relation to the Baltic Sea is presented on Figure 1-3, while plot of sample scores of F1 vs F2 and F3 vs F4 for bottom sediments visualized according to analogous criteria and moreover according to seasonality is presented on Figure 4-5.

The location of samples along F1 axis collected from fully connected ICOLLs proves that water is not as rich in Ho, Ir, Nd and Sm as those collected from partially connected or isolated coastal lakes and lagoons. Except for samples from Resko lake water collected from FC lakes create rather homogenous groups, while those from PC and I lakes are spread, especially according to concentration of Al, Fe, Mn, Ti, V and Yb. The highest dispersion along F2 axis is observed for Jamno indicating substantial anthropogenic impact due to water treatment plant operating nearby. Jamno lake is fed by Dzierżęcinka stream, major receiver of effluence from mentioned plant for Koszalin, which is supplied in drinking water coming from Tertiary and Cretaceous underground springs located in Mostowo.

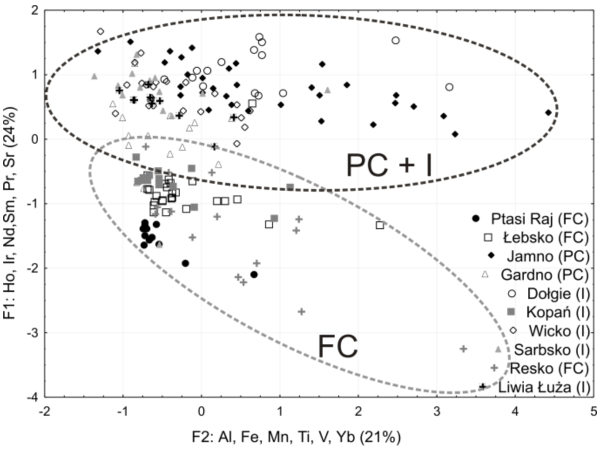

Figure 1. F1 (Ho, Ir, Nd, Sm, Pr and Sr) and F2 (Al, Fe, Mn, Ti, V and Yb) scores according to level of isolation (FC - fully connected, PC - partially connected, I - isolated) of ICOLLs.

Before being introduced to the water distribution system, raw water is deironized and demanganized. As a consequence, Fe and Mn are immobilized on the periodically backwashed absorption filters. After backwashing, the wastewater is dumped into the Dzierżęcinka river. That is why increased contents of Fe and Mn are observed in water collected in Jamno lake.

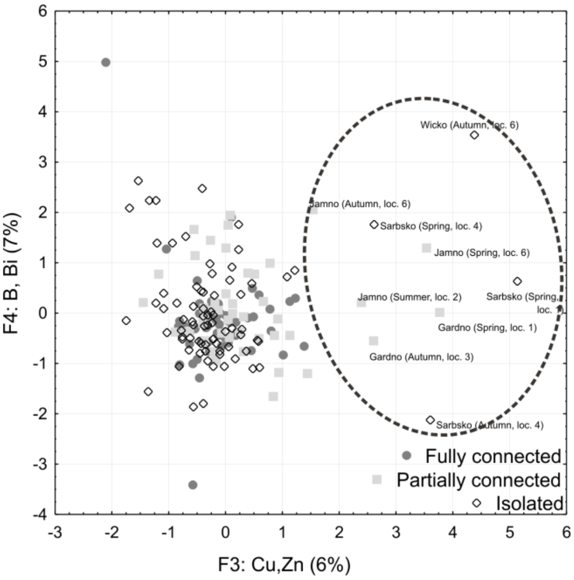

Figure 2. F3 (Cu, Zn) and F4 (B, Bi) scores according to level of isolation of ICOLLs.

Careful inspection of Figure 2 proves that, except for around 10 samples located mainly on the right side from the dominant "cloud", ICOLLs samples create relatively homogeneous and overlapping group. It suggests substantial similarity and seasonal independence of coastal lakes according to concentration of Cu, Zn, B and Bi. However, Figure 2 also revealed some unexpected sources of water contamination. F3 clearly distinguishes a single samples from Jamno, Gardno and Sarbsko lakes characterized by high concentration of Cu and Zn which were collected mainly in Spring and Autumn. Since the belt of northern Poland is a region free from commercial smelters and mines, which are commonly recognized as source of anthropogenic Zn, detailed inspection of sampling places became necessary. It revealed that, due to extraordinary natural and touristic values, some small wooden playgrounds or camping places were installed by local authorities in the close vicinity of water line. Surprisingly, installation of wooden swings and benches can explain local contamination by Zn, since such installation have to be preserved prior touristic season and winter against pests by the use of fertilizers and wood preservatives containing zinc.

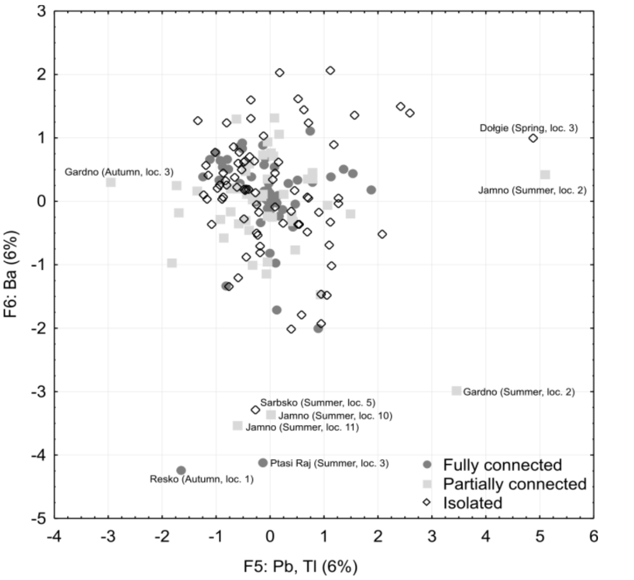

Figure 3. F5 (Pb, Tl) and F6 (Ba) scores according to level of isolation of ICOLLs.

Similar as above, ICOLLs' relation to the Baltic Sea, as well as seasonality, do not play any significant role in diversification of them according to Pb, Tl and Ba concentration, since dominant "cloud" of points represents samples collected from all types of ICOLLs. Having in mind that F5 and F6 explain only 12% of the total variance of the system (6% each of them) both factors explain variation of a single samples: three samples of the highest concentration of Pb and Tl and six samples of the highest concentration of Ba. Two of three samples characterized by the highest concentration of Pb and Tl were collected in the middle of the lakes in summer, while five of six samples characterized by the highest concentration of Ba were collected close to the bank in summer. Such phenomenon suggests that Ba deposited in bottom sediments could be released to water body when local temperature increases, however precise explanation should involve analysis of local stratigraphy and sediment's quality.

In contrast to water samples an abundance of heavy metals in bottom sediments shows significantly higher seasonal dependency. Dispersion of points presented on Figure 4 clearly distinguishes samples collected in Jamno lake which is partially related to the Baltic Sea. In this specific case the connection is artificially limited by a storm gate built to protect ecological habitats of the lake (Hesse *et al.*, 2013).

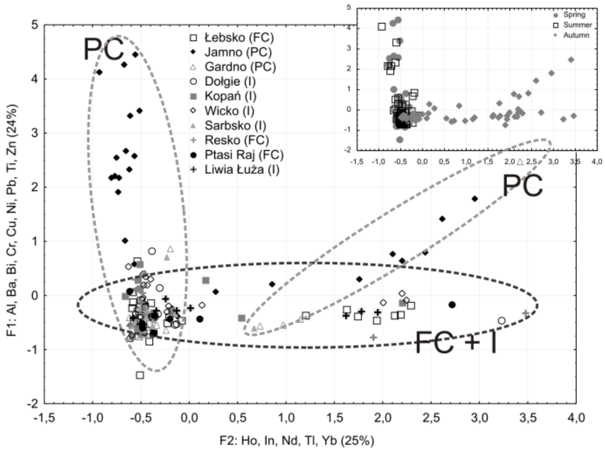

Figure 4. F1 (Al, Ba, Bi, Cr, Cu, Ni, Pb, Ti and Zn) and F2 (Ho, In, Nd, Tl and Yb) scores according to seasonality and level of isolation (FC - fully connected, PC - partially connected, I - isolated) of ICOLLs.

The location of Jamno sediments along F1 characterized by factor scores much higher than 1 and marked by vertical and right-hand skewed ellipses proves that these samples were more contaminated by heavy metals of the highest environmental concern (Cr, Cu, Ni, Pb and Zn) in comparison with all other sediments. For particular metals mentioned concentration increase was as follows: 1.37-1.86 for Al, Bi, Ni, Pb and Ti; 3.23 for Cu, 4.22 for Zn and 5.32-5.76 for Cr and Ba. Observed pattern confirms that aquatic ecosystems' pollution by heavy metals is mainly due to anthropogenic pressure and is not related to the level of isolation of the lake towards the Baltic Sea. The location of samples collected both, in fully connected and isolated lakes along F1, proves that these sediments were not as rich in Al, Ba, Bi, Cr, Cu, Ni, Pb, Ti and Zn as these collected in Jamno. Such conclusion is reasonable since projection of factor scores of FC and I lakes on F1 varies in the range between -1 and +1 indicating negligible influence of F1, which meaning in this case refers to heavy metals abundance. Figure 4 reveals an extraordinary seasonal variation of Ho, In, Nd, Tl and Yb concentration in bottom sediments of several Polish coastal lakes. Majority of samples projected along F2 and its highly positive factor scores were collected in Autumn. The characteristic feature of this part of the year on Polish coast is occurrence of heavy storms caused by strong western winds (Merchel, 2014). Winds of high velocity accompanied by sea storms cause not only the backflow of river water in coastal areas and changes in water levels in other coastal water reservoirs, they also induce the phenomena of underground sea water intrusions. Sea water intrusions are defined as the penetration of sea water into coastal water-bearing layers and bodies of surface water that have a permanent or temporary linkage to the sea. As a result of the intrusion of sea water, these types of aquatic ecosystems experience sudden increase in the concentration of selected chemical entities (Cieśliński *et al.*, 2009), chlorides and sodium in particular. Since concentration of Ho, In, Nd, Tl and Yb in sea water is measured usually as ng kg^{-1} (GERM, 2017) sea water intrusions could not be a dominant source of these metals in sediments, however we suppose that underground intrusions and sudden inflow of sea water cause vertical, turbulent mixing of sediments, and hence sediments rich in Ho, In, Nd, Tl and Yb are easy accessible in Autumn.

Similar interesting seasonal variation is revealed by factors scores dispersion presented on Figure 5. As could be seen bottom sediments collected from lakes of various connectivity toward the Baltic Sea create rather overlapping cloud, however some slight diversification appears according to seasonality.

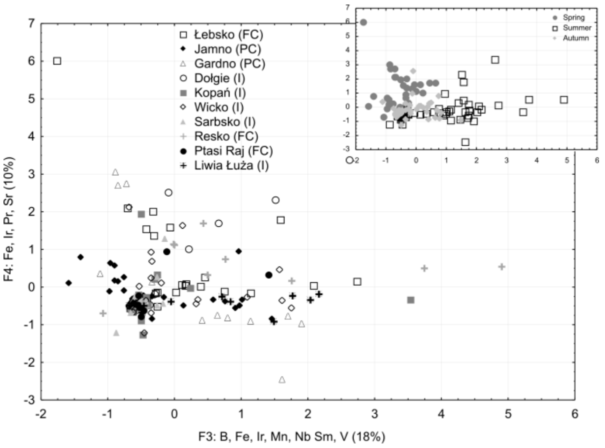

Figure 5. F3 (B, Fe, Ir, Mn, Nb, Sm and V) and F4 (Fe, Ir, Pr and Sr) scores according to seasonality and level of isolation (FC - fully connected, PC - partially connected, I - isolated) of ICOLLs.

Sediments collected in summer were more abundant with metals located close to each other in the periodic table (V, Fe and Mn) and lanthanides (Nd, Sm) than samples collected in spring, which were more abundant with Fe, Ir, Pr and Sr. It suggest that mutual equilibrium of metals' concentration depends on seasonal modification caused by changes of temperature, external inflow of sea water as well as vertical, turbulent mixing of sediment layers due to wave motion. Moreover, in case of fully connected lakes (in particular Resko and Łebsko) high concentration of Fe and Mn in water corresponds with high concentration in sediments.

Conclusions

The method used allowed a logical spatiotemporal grouping of heavy metals variation in water and bottom sediments of ICOLLs in northern Poland. An important factors impacting water quality are: (1) removal of seminatural compounds (Fe, Mn) by municipal water treatment plants located in the vicinity of feeding rivers as well as (2) local contamination caused by touristic equipment preservation against pests. Heavy metal abundance in bottom sediments depends on their presence in water and vary according to seasonality.

Acknowledgements

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