

# The potential impact of land use changes on heavy metal contamination in the drinking water reservoir catchment (Dobczyce Reservoir, south Poland)

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**Abstract:** To investigate and assess the effects of land use and its changes on concentrations of heavy metals (Pb, Zn, Cd, Cu, Mn, Ni, Fe) in the tributary of drinking water reservoir catchment, soils of different land use types (forest, arable land, meadows and pastures, residential areas), suspended sediment and bottom sediment were collected. Heavy metals were analyzed using atomic absorption spectrophotometry (AAS). The metal distribution pattern was observed, where Zn and Cd could be considered as main metal contaminants. The variation in the concentration level of Zn and Cd in studied soils showed the impact of pollution from anthropogenic activities. Also some seasonal variations were visible among the suspended sediment and bottom sediment samples which could be associated with land agricultural practices or meteorological conditions. The sediment fingerprints approach used for determining sources of the suspension in the catchment showed (Kruskal-Wallis H test,  $p < 0.05$ ), that only Mn and Ni were not able to be distinguished among the potential sediment sources. A multiple linear regression model described the relationship between suspended sediment and 4 types of soil samples. The results related suspended composition mostly to the samples from the residential land use. Considering the contemporary trend of observed changes in land use resulting in conversion of agricultural areas into residential and service structures these changes can be essential for the contamination of aquatic environment. This situation is a warning sign due to the rapid industrialization, urbanization and intensive agriculture in this region what can significantly affect the drinking water quality.

## Introduction

The problem of land use and land cover changes (LUCC) is one of the most widely discussed environmental issues in recent decades, and can be observed in many parts of the world (Yang et al. 2003). The mountain areas, especially the Carpathians recently underwent particularly intense structural transformation, mainly in agricultural production, infrastructure, and environmental changes in the structural space. In Eastern Europe, these transformations began during socio-economic changes after 1989. Moreover, the access to the European Union (for Poland in 2004) resulted in many alterations of natural and anthropogenic catchment processes. This situation caused, among the others, changes in the land use structure, both within the agricultural areas and non-agricultural lands, urban areas and technical infrastructure (Kopacz 2007, Twardy 2008, 2009). Political and economic fluctuations made agricultural areas less profitable. Moreover, a significant reduction in livestock population (sheep and

cattle) has been also observed, and such lands have been mostly reclassified for residential and service buildings. In many cases, almost a complete abandonment of agricultural use occurred, resulting in plant succession, and consequently, in afforestation of areas previously used for agricultural purposes (Kopacz et al. 2009, Kopacz and Twardy 2014, Twardy 2011). Kuemmerle et al. (2008) studied the abandonment of land in the Carpathians in a triangle of 18,000 km<sup>2</sup> bounded between the borders of Poland, Slovakia and Ukraine. In this study the substantial differences in abandonment among the countries between 1986 and 2000 have been noted: 20.7% in Slovakia, 13.9% in Poland, and 13.3% in Ukraine. Also, Muller and Kuemmerle (2009) estimated that 21% of land in Arges County (the Carpathian region in Romania) was abandoned between 1900 and 2005. In recent years the activity from some local and government entities, e.g. The Agency for Restructuring and Modernization of Agriculture (ARMA), Malopolska Agricultural Advisory Centre, has been observed to reverse this trend in Poland. For example, in the Polish

Carpathian regions these agencies, through their activities, try to encourage farmers to continue production, not to set aside and abandon arable land, and encourage them to seek funding for the agricultural production. Among their activities are: implementing other entities in rural development, expert advice in agricultural problems, organizing trainings, conferences, meeting concerning mainly sustainable agriculture, water and soil protection, and organic farming (Myslenice County 2017).

Type of land use and its development are essential for the quantity and quality of soils, and subsequently for the quantity and quality of the material transported from the catchment to the aquatic environment. Especially, in the areas where surface run-off is a major concern during snow melt and rain periods due to the catchment slope, which is an important case for the Carpathian region. The process of washing out of substances from the soil surface depends on the multiple factors, including geological, hydrological, and meteorological settings in the catchment. However, the anthropogenic factors, including land use in the catchment (e.g., agricultural, urban, industrial, residential, and commercial) play also the pivotal role in transfer of pollutants from the catchment to the receivers (Gajewska and Wargin 2010, Szalinska et al. 2010). These pollutants, especially heavy metals, have become an important environmental issue in developed countries due to significant differences between particular land uses (Adriano 2001). Knowledge of heavy metals concentrations in different land use types is of critical importance in assessing human impact on metal concentrations in soils (Chen et al. 2005a).

Heavy metals are introduced into the environment through different pathways. Biogeochemical processes, including sorption/desorption, complexation, dissolution/precipitation, and uptake/release by biota, control the mobility of heavy metals and thus their residence time in soils, water and bottom sediments (Carillo-González et al. 2006, Reeder et al. 2006). Heavy metals tend to accumulate especially in soils and bottom sediments (Foster and Charlesworth 1996) because of their affinity for sorption processes. The solid-solution partitioning in soils is mainly controlled by pH, redox potential, clay and soil organic matter (SOM) content, and the concentration of complex organic or inorganic ligands and competing cations (Wijngaard et al. 2017). Dissolved heavy metals are transported to surface waters via several hydrological pathways (e.g. through surface run-off, evaporation, and infiltration) (Gajewska and Wargin 2010). Therefore, detailed assessment of contamination within the contributing catchment is especially important when the quality of drinking water is at stake (Bibby and Webster-Brown 2004). Also, bottom sediments can play a pivotal role in determining quality of drinking water reservoirs, since they act as carriers and sinks for contaminants, reflect history of pollution, and provide a record of catchment inputs into ecosystem. Furthermore, sediments with high levels of contaminants may be a secondary source of environmental pollution (Lacorte et al. 2006).

Numerous studies have demonstrated the presence of heavy metal concentrations in suspended sediment and bottom sediments, and they can be sensitive indicators of contaminants in aquatic systems (Chao et al. 2009, Jain and Sharma 2001). In addition, some studies (e.g. Chao et al. 2009, Collins et al. 1997, Dessouki et al. 2005, Kamala-Kannan et al. 2008, Koroluk and de Boer 2007, Salomons and Forstner 1980,

Walling 2005) have also attempted to quantify the sources of suspended sediment transported in river systems using heavy metals. This method is based on comparison of geochemical properties of suspended sediment samples with the samples of soil from the catchment. Among the geochemical markers (*sediment fingerprinting*) commonly used are heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Zn). Such composite fingerprints permit a representative and consistent method of verifying sediment origin, and often allow for the determination of different sources (Collins and Walling 2002).

The aim of this study was the assessment of heavy metals contamination (Pb, Zn, Cd, Cu, Mn, Ni, Fe) in soils of different land use types (forest, arable land, meadows and pastures, and residential areas), suspended sediment, and bottom sediments in the tributary of drinking water reservoir, the Wolnica Stream catchment. Authors attempted to find a relationship between heavy metal concentrations in soils of different land use types, suspended sediment, and bottom sediments in the Wolnica Stream catchment using geochemical tracers (*sediment fingerprints*). They also determined the contemporary trend of observed changes in land use and its impact on the Wolnica Stream catchment, and primarily the drinking water reservoir.

## Study area

The Wolnica Stream is the left tributary of the Dobczyce Reservoir and flows into the northern arm of the reservoir which is situated 30 km south of the city of Cracow (around 800,000 inhabitants). The dam reservoir was built between 1984–1987 as the main source of potable water for Cracow. The water intake with pumping station is located 61.4 km from the mouth of the Raba River on the left bank of the reservoir. The reservoir is supplied by the Raba River waters (90% of the total inflow) and its tributaries. The waters of two other streams – the Wolnica and the Trzemieszianka contribute about 2% and 4%, respectively. Five other small streams, the Bulinka, Ratanica, Brzezówka, San, and Dębniek add a total of approximately 2.5% (Pawelek and Spytek 2008, Sadag et al. 2016).

The total catchment area of the Dobczyce Reservoir is about 768 km<sup>2</sup> while its immediate watershed is about 72 km<sup>2</sup>. The sources of the Raba River are in the Carpathian belt of the Gorce Mountains. The Beskids part of the catchment basin of the Dobczyce Reservoir is composed of sandstone shale formations. Within the study area the flysch is covered with the Quaternary sediments which consist of loess and glacial fluvial clays, sands, and pebbles. The youngest deposits in the Wolnica Stream and other tributaries are alluvial ones. The soils formed on the flysch rocks are differentiated due to the relief of the terrain and the intensity of morphogenetic processes. A soil cover on the left bank of the reservoir is mostly loess loam type: gley soil (Stagnic Luvisols) and fallow soil (Haplic Luvisols) (Skiba et al. 1998). This kind of soil, due to its dusty-grained character, is very susceptible to the water erosion process and can add a significant volume of suspended sediment to reservoir water. However, loamy sand and sandy clay loam soils belonging to Podzols and Dystric Cambisols dominate on the right bank of the Dobczyce Reservoir. Loess soils prevail only in the area of Wolnica Bay (Drzewiecki and Mularz 2008, Szarek-Gwiazda and Sadowska 2010). In the land

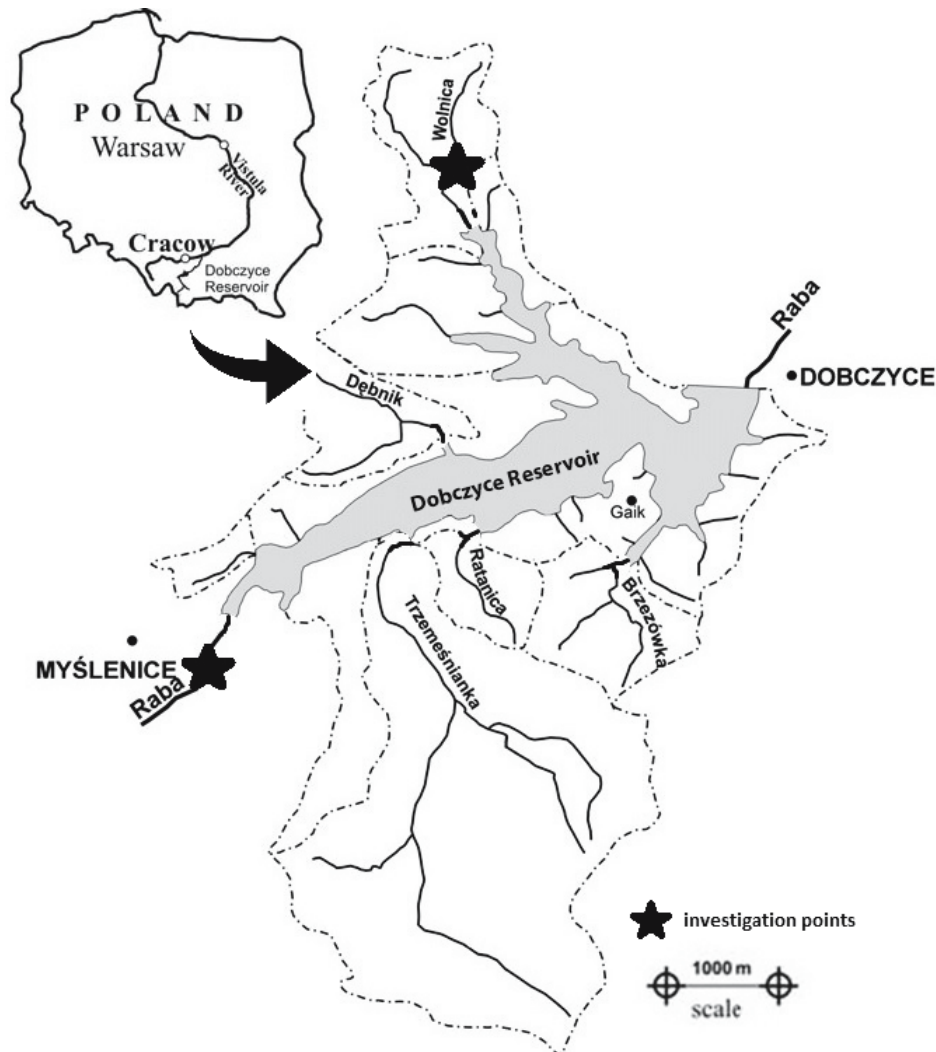


Fig. 1. Localization of the Dobczyce Reservoir with its tributaries and investigation points (Pawelek and Spytek 2008)

use of the Wolnica Stream catchment basin dominate arable land, meadows and pastures which constitute about 42.0%, while forests only 9.4%. The built-up areas (3.1%) have the smallest contribution of land use structure (Copernicus 2017). In the Wolnica Stream catchment basin, forests constitute of *Quercus L.*, *Fagus sylvatica L.*, *Pinus L.*, *Picea A. Dietr.*, *Abies Mill.*, and *Larix Mill.* Predominating crops in arable land of these areas are radishes and potatoes. Plants located on the meadows and pastures are mostly deciduous trees (e.g. *Robinia pseudacacia*), bushes (e.g. *Philadelphus coronarius*, *Cornus alba*, *Hippophaë rhamnoides*), and other species (e.g. *Bromus secalinus*, *Dactylis glomerata*). However, plants associated with meadows and pastures coastline are rushes and overwater communities (e.g. *Polygono-Bidentetum*, *Typhetum latifoliae*, *Filipendulo-Geranium*, *Scirpetum sylvatici*) (Trzcinska-Tacik and Stachurska-Swakon 2001). Residential and commercial buildings reflect to single-family buildings, and small industrial plants.

The Wolnica Stream catchment basin is subjected to agricultural land use where mineral fertilizers are a main source of water reservoir contamination. Therefore, the reservoir is subjected to the effects of a considerable contaminant load delivered from its catchment i.e. eutrophication. Despite

the relatively great distance from urban and industrial agglomerations, atmospheric precipitation in the area of the reservoir is threatened by emissions from the metallurgical industry in Cracow and two power plants located in Skawina and Cracow (Szarek-Gwiazda 2013).

## Materials and methods

### Sample collection and processing

Soil samples (0–5 cm) were collected by hand into polyethylene plastic bags (~200 g) from the Wolnica Stream catchment (4 km north of the reservoir) in March, May, September, and November of 2017. The location of particular soil sampling sites corresponded to a different land use: forest (F), arable land (A), meadows and pastures (M), and residential areas (R). During sampling period, 1 sample was collected per month from 4 different land uses (16 soil samples in total). To increase the representativeness of the individual samples composite soil samples were collected from each sampling plot. An individual sample was composed of 5 subsamples, collected within 10×10 m<sup>2</sup> plot (located on crossing diagonals: four in the corners and one at the crossing point). The sampling scheme took into account sites representing the most relevant



characteristics of the environment and each soil type. The material of each soil sample was wet sieved through a 63  $\mu\text{m}$  mesh, air dried, disaggregated using a pestle and mortar, and stored at room temperature until further laboratory analysis.

Furthermore, to illustrate the possibility of metal transfer from the catchment to the aquatic environment, samples of the suspended sediment (SS) and bottom sediments (BS) were also taken into consideration. All samples were collected during the same sampling days (1 sample of SS and BS per month, 8 samples in total). SS was retained with the use of *time-integrated sampler* (Banasik and Hejduk 2005, Phillips et al. 2000), which is permanently installed in the selected profile on the Wolnica Stream. Its use and effectiveness have been described elsewhere (Zemelka and Szalinska 2017). Briefly, its shape and size enable the inflow velocity reduction by a factor of approx. 600, thereby promoting the deposition of suspended particles (<63  $\mu\text{m}$ ) inside of the device. SS samples were collected in plastic containers (20  $\text{dm}^3$ ), transported to the laboratory where recovered by sedimentation and centrifugation (5 min at 4000 rpm), then air dried and disaggregated using a pestle and mortar. Afterwards, this material was subjected to the laboratory analysis. Surface BS samples were also taken manually to polyethylene plastic bag (~100 g) in the vicinity of the *time-integrated sampler*. Sediment samples were processed according to the same protocol as the soil samples.

To compare metal contamination level in the Wolnica Stream with the main Dobczyce Reservoir tributary catchment, samples of soil, SS, and BS samples were collected from the Raba River catchment. Soil samples (0–5 cm) were collected in March and May 2017, and the location of particular sampling sites corresponded with the following land use: A, M, and R (6 soil samples in total). Likewise, the samples of SS and BS were also collected (2016, and 2017), however the sampling procedure differed slightly in this case. SS samples were collected manually in the Raba River estuary to plastic containers (10  $\text{dm}^3$ ). All further material processing was performed in the same way as described above for the Wolnica Stream samples.

### Chemical analysis

Soil, SS, and BS were subjected to the same laboratory protocol. Briefly, dry samples (0.5 g) were mineralized in 10 ml of 65%  $\text{HNO}_3$  Suprapur® (Merck) in a closed microwave system (Milestone Start D Microwave Digestion System) at 175°C for 10 min using Method 3051 (USEPA 1994). Heavy metal (HM) measurements (Pb, Zn, Cd, Cu, Mn, Ni, Fe) were performed with use of atomic absorption spectrophotometry (the Thermo Scientific iCE 3500). Blanks and standards were run for every sample batch to ensure the precision of measurements. Method validation and quality control samples were done by using a standard certified reference lake sediment material (LKSD-4, CCRMP, Canmet, Canada).

### Data analysis

The obtained data set was compared to the geochemical background for sedimentary rocks given by Kabata-Pendias and Pendias (1993): Zn 120, Cd 0.35, Pb 40, Cu 60, Ni 90, Mn 1000, Fe 48000 mg/kg dry weight. General statistics in this study was produced using Excel v. 2007. To compute significant differences in HM among the soil samples, SS, and

BS samples, and also to observe differences in time between sampling months the ANOVAs followed by Tukey's multiple comparison test were performed. The approach to distinguish between sources contributing to the SS composition (fingerprinting method) was performed with use of Kruskal-Wallis H test and the multiple regression model (Statgraphics XVII).

## Results and discussion

Average concentration of HM in soil samples of the Wolnica Stream (Table 1, Figure 1) varied within the broad limits, especially for Zn (35.8–168 mg/kg) and Cd (0.160–1.04 mg/kg). Moreover, for these two metals the geochemical background values were frequently exceeded (Kabata-Pendias and Pendias 1993). For the remaining investigated metals the measured concentrations were below the adopted standard values, except for Pb in the March sample from the arable land soil. A similar metal distribution pattern was also observed for samples from the Raba River catchment (Table 2), where Zn and Cd also could be considered as main metal contaminants. The variation in concentration level of Zn in studied soils showed the impact of pollution from anthropogenic activities rather than the lithogenic ones. The main sources of Zn are pesticides, especially fungicides, and fertilizer use has been implicated in elevated Zn concentrations in soils (Taylor and Percival 2001). However, the concentration of Cd is caused to a great extent by the land application of phosphate fertilizers that contain among others Zn. In addition, wastewater is likely important source of Cd in soils (Taylor 1997).

The measured metal concentrations for soil samples were also compared with the guideline values given by the Polish Ministry of the Environment Regulation from Sep. 1, 2016 (Polish Ministry of the Environment 2016). According to this act the total permissible concentrations of HM were specified in the following soil types (0–0.25 m): residential areas (class I), arable land, meadows and pastures (class II), and forest (class III). Taking into consideration the obtained data, including investigated metals and the respective types of land, it should be observed that acceptable levels were not exceeded neither in the Wolnica Stream, nor the Raba River catchments.

Among the examined land use types within the Wolnica Stream catchment some differences were visible, however not at a significant level (ANOVA,  $n=108$ ,  $p>0.05$ ). Generally, the observed metal concentrations were low for the F soils, and high for the A samples from the arable land. A similar pattern was also observed in soils from the Slovakian part of Carpathians (Wilcke et al. 2005). Samples collected (1994, and 1999) from arable, meadows and pastures, and forest areas displayed visibly higher concentrations (almost 20%) than in the current study, however the decreasing concentration order was as detected for the Wolnica Stream catchment area: arable land > meadows and pastures > forest.

Since a surface runoff promotes contaminant transport from soils to the aquatic environment, the investigated HM were also found in SS and BS samples collected from the Wolnica Stream and the Raba River. SS transported by a stream usually represents a mixture of material derived from different locations and source types. Therefore, HM contents

**Table 1.** Heavy metal average concentrations [mg/kg] in soils from the Wolnica Stream catchment (2017)

Date	Type of soil	Pb	Zn	Cd	Cu	Mn	Ni	Fe
March	F	27.7	35.8	0.176	7.32	104	6.76	9556
	A	<u>43.3</u>	<u>168</u>	<u>1.04</u>	25.4	553	26.4	28117
	M	36.0	<u>154</u>	<u>1.00</u>	21.4	452	27.2	24407
	R	14.3	55.3	<u>0.488</u>	10.1	309	9.72	11607
May	F	39.2	54.7	0.160	4.44	168	6.84	8856
	A	16.7	60.6	<u>0.415</u>	9.46	258	11.0	12804
	M	25.0	<u>123</u>	<u>0.527</u>	15.1	189	11.0	13620
	R	26.7	<u>131</u>	<u>0.555</u>	16.0	410	12.8	10464
Sept.	F	31.7	43.6	0.244	7.10	258	6.84	11399
	A	30.2	<u>137</u>	<u>0.619</u>	14.8	355	16.4	18869
	M	11.3	53.7	<u>0.372</u>	9.25	267	9.13	11932
	R	18.8	<u>167</u>	<u>0.403</u>	15.0	318	14.6	13756
Nov.	F	36.6	37.5	0.220	6.55	161	4.64	9355
	A	23.9	101	<u>0.803</u>	12.7	303	14.6	15892
	M	15.5	61.8	<u>0.447</u>	10.9	328	10.5	13777
	R	24.9	<u>148</u>	<u>0.581</u>	15.4	374	13.1	12624
Geochemical bcg. level		40.0	120	0.350	60.0	1000	90.0	48000

Explanation:

a) underlined values – values exceeding the geochemical background (Kabata-Pendias and Pendias 1993)

b) F – Forest, A – Arable land, M – Meadows and pastures, R – Residential area

**Table 2.** Heavy metal average concentration [mg/kg] of heavy metals in soils from the Raba River catchment (2017)

Date	Type of soil	Pb	Zn	Cd	Cu	Mn	Ni	Fe
March	A	30.0	118	<u>0.755</u>	30.4	675	45.1	20759
	M	3.42	26.9	0.10	8.22	418	17.9	7368
	R	37.8	183	<u>0.958</u>	33.3	670	35.2	23559
May	A	25.9	80.9	<u>0.637</u>	17.6	334	17.9	13410
	M	6.98	50.8	0.137	11.3	228	20.6	14017
	R	19.3	81.3	0.344	18.1	405	40.8	18691
Geochemical bcg. level		40.0	120	0.350	60.0	1000	90.0	48000

Explanation:

a) underlined values – values exceeding the geochemical background (Kabata-Pendias and Pendias 1993)

b) A – Arable land, R – Residential area, M – Meadows and pastures

in SS (Table 3) were predominantly in similar ranges as in the soils from the investigated catchments. The correlation coefficient matrix between HM in soils and SS in all studied seasons showed that results were positively correlated with each other and correlations were statistically significant ( $p < 0.01$ ) displaying similar geochemical features. Moreover, the concentrations of HM in SS were noticeably higher than in BS (Table 4).

Some seasonal variations were visible among the SS and BS samples which could be associated with the land agricultural practices or meteorological conditions. In spring and autumn (March, September) where the use of soil fertilization and farm machinery for crops is prevailing, an increase of concentrations

was observed, while a decrease in May and November could be related to the elevated precipitation. Generally, HM concentration levels were below values set by geochemical background, except for Zn, Cd, and Mn for SS, and Cd for BS. BS metal concentrations were also in agreement with previous findings for the Wolnica Stream, and the Dobczyce Reservoir (Reczynski 2010, Szarek-Gwiazda et al. 2011, Szarek-Gwiazda 2013, Szlapa et al. 2017).

Since the SS composition is commonly used for determining sources of the suspension in the catchment using geochemical tracers (*sediment fingerprints*) (Belmont et al. 2014, Walling 2005, Walling et al. 2008) such approach was also adopted for the Wolnica Stream catchment. The measured

**Table 3.** Heavy metal average concentrations [mg/kg] in suspended sediment of the Wolnica Stream (2017) and the Raba River (2016–2017)

Date	Area	Pb	Zn	Cd	Cu	Mn	Ni	Fe
March	W	15.2	<u>296</u>	0.258	14.2	<u>1064</u>	15.2	16702
May		13.7	110	0.184	9.54	497	11.0	12446
Sept.		13.5	<u>385</u>	<u>0.462</u>	21.2	<u>2364</u>	18.8	21875
Nov.		11.8	93.1	<u>0.439</u>	14.1	840	16.6	18464
2016–2017	R	13.0	88.9	0.212	24.9	905	55.6	24415
Geochemical bcg. level		40.0	120	0.350	60.0	1000	90.0	48000

**Explanation:**

a) underlined values – values exceeding the geochemical background (Kabata-Pendias and Pendias 1993)

b) W – Wolnica Stream, R – Raba River

**Table 4.** Heavy metal average concentrations [mg/kg] in sediments of the Wolnica Stream (2017) and the Raba River (2016–2017)

Date	Area	Pb	Zn	Cd	Cu	Mn	Ni	Fe
March	W	10.3	44.4	0.112	7.66	393	10.9	11098
May		14.0	45.1	0.161	7.91	281	11.8	11739
Sept.		9.45	56.9	<u>0.416</u>	11.0	619	14.3	17387
Nov.		4.99	44.2	0.290	8.83	329	12.3	11863
2016–2017	R	16.6	93.6	0.297	30.3	801	67.9	27443
Geochemical bcg. level		40.0	120	0.350	60.0	1000	90.0	48000

**Explanation:**

a) underlined values – values exceeding the geochemical background (Kabata-Pendias and Pendias 1993)

b) W – Wolnica Stream, R – Raba River

metals were considered as conservative tracers in the current study and were statistically tested to distinguish if they exhibit significant differences among the sources (land use types). Since, metal concentrations for all the soil and SS samples did not exhibit significant differences (ANOVA,  $n=135$ ,  $p>0.05$ ) with sampling months, subsequently the following analyses were run on the whole dataset. The results showed (Kruskal-Wallis H test,  $n=135$ ,  $p<0.05$ ), that only Mn, and Ni were not able to be distinguished between the potential sediment sources in an unequivocal manner (sampling site had no significant influence on Mn and Ni concentration), and subsequently were removed from the data set. To describe the relationship between SS, and 4 types of soil samples (F, A, M, and R) a simple multiple stepwise regression model was adopted, due to the limited size of the data. The results of fitting a multiple linear regression model to describe the relationship between SS and F, A, M, and R samples (treated as independent variables) resulted in a following equation:  $SS = -36.3378 + 1.45055 \cdot R$ , relating suspended composition mostly to the samples from the residential land use. The  $r^2$  statistic indicated that the model as fitted explained 98.8792% of the variability in SS samples. Considering a very limited number of sediment fingerprints applied in the current study the modelling results

can be regarded as only preliminary. However, considering the contemporary trend of observed changes in land use resulting in conversion of agricultural areas into residential and service structures they can be essential for the contamination of aquatic environment. Significantly increased amount of contaminants coming from urbanized areas (e.g. stormwater, domestic wastewater) discharged into the reservoir catchment can contribute to disrupting the ecological balance (reduction in the number of living organisms and biodiversity), as well as quantitative changes, and deterioration of water quality (Molenda 2006).

## Conclusions

The political and socio-economic changes related to the transition from the communist system to a free-market economy, then to the accession of Poland to the European Union had profound impacts on less profitability of agriculture production in the Polish Carpathians. The general trend was observed resulting in the increase of abandonment of land as well as decrease of population dependent on agriculture. Then, the main sources of income for the study area inhabitants were off-farm activities (construction, services, and agritourism).

These activities have contributed to future land use change in the Carpathian region and more attention was paid to the quantity and quality of soils, and subsequently to the quantity and quality of the material transported from the catchment to the aquatic environment. The investigated impact on HM soil contamination in the tributaries of drinking water reservoir catchment (the Wolnica Stream and the Raba River) considered as Zn and Cd pollution, particularly in arable land. Such pollution originated mainly from antropogenic activities, the usage of fungicides and phosphate fertilizers. Moderate contamination of the environment was found in the Wolnica Stream catchment with the following order of degree of contamination: arable land > meadows and pastures > forest. HM were also found in SS and BS samples collected from the Wolnica Stream and the Raba River. Thus, our study confirmed that surface runoff promoted contaminant transport from soils to the aquatic environment. Furthermore, agricultural practices or meteorological conditions had an impact on prevailing increase of HM concentrations in SS and BS. Also, the *sediment fingerprints* approach used for determining sources of suspension in the catchment and a multiple linear regression model indicated the origin of SS to residential land use. Considering the contemporary trend of observed changes in land use resulting in conversion of agricultural areas into residential and service structures they can be essential for the contamination of aquatic environment. This situation is a warning sign due to rapid industrialization, urbanization and intensive agriculture in this region. Counteracting these processes requires constant monitoring of HM, and above all, enforcement of their removal from waste disposal and monitoring other potential pollution sources which can contaminate drinking water in the Dobczyce Reservoir.

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## Potencjalny wpływ zmian użytkowania gruntów na zanieczyszczenie metalami ciężkimi w zlewni zbiornika wody pitnej (Zbiornik Dobczycki, południowa Polska)

**Streszczenie:** Celem pracy była ocena wpływu użytkowania gruntów i ich zmian na stężenia metali ciężkich (Pb, Zn, Cd, Cu, Mn, Ni, Fe) w dopływie zlewni zbiornika wody pitnej. Do badań pobrano próbki gleb z różnych typów użytkowania gruntów (las, grunty orne, łąki i pastwiska, tereny zabudowane), rumowiska unoszonego oraz osadów dennych. Metale ciężkie oznaczono za pomocą Atomowej Spektroskopii Absorpcyjnej (ASA). W badanych próbkach zaobserwowano zmienność stężeń metali w zależności od sposobu użytkowania gruntów. Otrzymane wyniki świadczą również, że główne zanieczyszczenie metaliczne w zlewni stanowią Zn i Cd. Wśród próbek rumowiska unoszonego oraz osadów dennych widoczne były pewne wahania sezonowe, które mogły być związane z działalnością rolniczą lub warunkami meteorologicznymi. Zastosowana do określania źródeł zawiesiny w zlewni metoda sediment fingerprints (test Kruskal-Wallis H,  $p < 0,05$ ) wykazała, że spośród badanych



metali jedynie Mn i Ni nie umożliwiają rozróżnienia potencjalnych źródeł pochodzenia rumowiska unoszonego. Pozostałe metale zostały zatem wykorzystane do opisanía zależności między rumowiskiem a 4 typami próbek gleb za pomocą modelu regresji wielokrotnej. Model ten wykazał związek zanieczyszczenia próbek rumowiska metalami z zanieczyszczeniem gleb z terenów zabudowanych. Biorąc pod uwagę zaobserwowany współczesny trend zmian w użytkowaniu gruntów, prowadzący do przekształcania obszarów rolniczych w obszary mieszkalne i usługowe, może on istotnie wpływać na zanieczyszczenie środowiska wodnego i jakość wody pitnej. Taka sytuacja jest znakiem ostrzegawczym ze względu na szybkie uprzemysłowienie, urbanizację i intensywną gospodarkę rolną w tym regionie.